

Semiclassical molecular dynamics simulations of ultrafast photodissociation dynamics associated with the Chappuis band of ozone

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In this paper we investigate the nonadiabatic ultrafast dynamics of interconversion between the two lower lying excited states of $^1A''$ symmetry ($1^1A''$ and $2^1A''$) of ozone following photoexcitation of the molecule in the gas phase with visible light. Our algorithm involves a semiclassical initial value representation method which is able to describe electronically nonadiabatic processes within the time dependent picture through the quantization of the classical electron–nuclear model Hamiltonian of Meyer and Miller [J. Chem. Phys. **70**, 7 (1979)]. We explore the capabilities of these techniques as applied to studying the dynamics of a realistic reaction of photodissociation on full *ab initio* electronic potential energy surfaces. Our semiclassical results provide an intuitive understanding of the most fundamental dynamical features involved in the process of predissociation, such as decay and recurrence events, as well as an interpretation of experimental studies of the Chappuis band of ozone in the frequency domain. © 1998 American Institute of Physics. [S0021-9606(98)00602-3]

I. INTRODUCTION

Understanding the molecular mechanisms of relaxation that produce broad and structureless electronic absorption spectra of polyatomic systems is a central problem in chemical dynamics, since the spectral consequence of these ultrafast relaxation processes is to mask the structural and dynamical information necessary to formulate molecular level descriptions of chemical processes. These mechanisms are also ideally suited to detailed investigation using new advanced theoretical and computational methods for treating electronically excited state complex reaction dynamics. This paper reports the first application of these new simulation methods^{1,2} to a real molecular system, the ultrafast photodissociation dynamics associated with the Chappuis band of ozone.

The photodissociation of ozone has been extensively investigated both theoretically and experimentally,^{3–19} not only because of its importance in atmospheric chemistry, but also because of its interesting electronic spectroscopy which provides a platform for studying the more fundamental aspects of photodissociation reaction dynamics. Perhaps the most sophisticated experimental study of dynamics associated with the Chappuis band of ozone has been the work of Chen *et al.*⁹ who developed a zero-background, multiplex-selected femtosecond transition-state spectroscopic technique that allowed direct visualization of the wave packet motion. However, despite the rich information content in the experimental data of this powerful transient stimulated emission pumping (TSEP) technique, the signals are the result of complicated dynamics of a polyatomic system, the details of which cannot be extracted by a cursory examination of the results. It is, thus, essential to combine experimental studies with theoret-

ical simulations that face the challenge of yielding a comprehensive understanding of the underlying dynamics.

In recent years, there has been significant progress in the development of a wide variety of quantum and mixed quantum-classical methods for describing chemical/molecular dynamics, including full quantum basis set or grid based formulations,^{20,21} path integral methods,^{22–27} Monte Carlo algorithms,^{28,29} time dependent self-consistent field integrators,^{30–43} Gaussian wave packet and other semiclassical techniques,^{44–60} and the reduced density-matrix approach.^{61–66} For dealing specifically with electronically nonadiabatic multidimensional coordinate reaction dynamics on realistic potential energy surfaces (PESs), the methods of choice have been effective path methods^{67–73} and surface-hopping techniques.^{74–80}

Surface-hopping methods have been successfully implemented in a variety of simulation studies of ultrafast dynamics of photodissociation.^{81–86} Although nuclear phase coherences were in general handled only on the basis of rather crude approximations and intramolecular couplings were completely disregarded, these approaches have nevertheless been found to be reasonable approximations for modeling the nonadiabatic dynamics of photodissociation of neutral and ionic diatomic molecular chromophores embedded in solids, liquids, and clusters. Furthermore, these surface hopping simulations showed that the introduction of *ad hoc* stochasticity did not introduce any serious problem in the ultrafast dynamics of relaxation when the hops took place at avoided crossing points, where the initial and final PESs had almost the same energy and topology. However, there are situations in polyatomic chromophore systems, such as conical intersections,⁸⁷ where couplings among the different modes of the molecule make the two surfaces involved in the process of interconversion significantly different, and vi-

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bronic coupling can give rise to new types of phenomena with no counterpart in diatomic systems. Under these circumstances the reliability of surface hopping techniques may decrease with the number of hops and the size of the energy gaps at the moment of transitions associated with distinct changes of electronic character.

Effective path methods propagate nuclear trajectories that are completely deterministic, like ordinary classical trajectory methods, except that they account for the multiple surfaces by means of an average potential.⁸⁸ As such, these methods have the advantage of not having to deal with the problems associated with discrete hops⁸⁹ from one adiabatic surface to another, but in their simplest version have the disadvantage of leading to unphysical asymptotic mixed final states.⁷⁴ They also share with surface hopping techniques the limitations with regard to the omission of nuclear coherence effects.

The purpose of this paper is to present the implementation of a new computational approach for treating nonadiabatic dynamics^{1,2} to the investigation of the ultrafast relaxation dynamics of ozone which, according to large scale *ab initio* calculations,⁵ involves the two lower lying excited states of $^1A''$ symmetry ($1^1A''$ and $2^1A''$), which are coupled by a conical intersection responsible for the broad and diffuse Chappuis band in the visible region of the absorption spectra. Our algorithm involves a semiclassical initial value representation (SC-IVR) method which is able to describe electronically nonadiabatic processes within the time dependent picture through the quantization of the classical electron–nuclear model Hamiltonian of Meyer and Miller.⁶⁸ Applications of this method to the three model problems suggested by Tully for testing nonadiabatic dynamics,⁷⁴ and to a spin boson model problem for dissipative systems show that it provides a realistic description of electronically nonadiabatic dynamics in a variety of situations.^{1,2}

In the original formulation of Meyer and Miller⁶⁸ a classical model for the electronic degrees of freedom in a molecular collision system was obtained and combined with the usual classical description of the nuclear motion to provide a complete classical model for the electronic and nuclear degrees of freedom. The present approach^{1,2} corresponds to quantizing this model semiclassically according to the Herman–Kluk (HK) IVR method.⁵⁵ The resulting SC-IVR model is similar to other effective path methods in that, unlike surface hopping methods, the trajectories evolve deterministically on an average PES according to the classical equations of motion for all degrees of freedom, electronic and nuclear. It differs from other effective path methods in that different electronic transitions have different nuclear trajectories because of the way the SC-IVR approach imposes boundary conditions on the classical trajectories. Like other semiclassical initial value representation methods, it aims to provide a more tractable alternative to exact quantum mechanical methods for dynamics calculations, as well as an intuitive understanding of complex quantum dynamics associated with chemical reactions in terms of classical mechanics, where quantum coherence effects are included correctly

and naturally for both electronic and nuclear degrees of freedom. Though this extension of the method removes the drawbacks inherent in classical path methods, there is the nontrivial question as to whether it can be efficiently implemented since it in general involves the evaluation of a high dimensional integral with an oscillatory integrand. It is shown in this paper, however, that the HK methodology, together with stationary phase Monte Carlo methods, can indeed be effectively used to evaluate these initial value integrals for ultrafast photodissociation dynamics of a small polyatomic system. Furthermore, we show that although converged calculations of the absorption spectra require the evaluation of quite a large number of trajectories (100 000 trajectories), most of the physics of the problem can be well understood from the analysis of the dynamics of a small ensemble of trajectories (50 trajectories).

The aim of these preliminary studies of photodissociation dynamics in the gas phase is not only to develop an understanding of how intramolecular vibronic coupling induces ultrafast nonadiabatic processes of interconversion (characteristic of higher excited electronic states of polyatomic molecules and responsible for rather broad and diffuse spectroscopic bands), but also to explore the capabilities of these semiclassical methods for studying the dynamics of realistic reactions on full *ab initio* electronic potential energy surfaces. In future applications, our semiclassical simulations will be coupled to the diatomics-in-molecules (DIM) methodology for electronic structure calculations, in order to develop a microscopic understanding of how perturbational effects of surrounding solvent atoms influences the potential energy surfaces of the polyatomic chromophore and changes nuclear dynamics over these complicated surfaces. According to previous simulation studies of photodissociation dynamics in other systems,^{82,85,86} the presence of the condensed phase environment can in principle introduce off-diagonal matrix elements and break the symmetry of the diabatic electronic states enhancing nonadiabatic transitions responsible for predissociation. Remarkably, perturbational effects have been observed experimentally in condensed phase absorption spectra of ozone for more than 50 years,^{90,91,8,92} however they have not been sufficiently investigated as to understand the possible effects of condensation on the photochemistry of ozone which might have a significant role in future atmospheric models.

The paper is organized as follows: In Sec. II we first outline our semiclassical approach for modeling the dynamics of photodissociation and the calculation of the absorption spectra. Section III then summarizes our results and compares them with the experimental findings and the results of full quantum calculations, followed by a detailed analysis of how the various spectroscopic features are associated with the phase space dynamics of nuclear and electronic variables. Section IV summarizes and concludes.

II. METHODS

A. Semiclassical approach

The total photoabsorption cross section $\sigma(\lambda)$ as a function of the photolysis wavelength λ is given by the Fourier transform of the survival amplitude (or autocorrelation function) $\xi(t)$,

$$\sigma(\lambda) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt \xi(t) e^{i\omega t}, \quad (2.1)$$

with $\omega = 2\pi c/\lambda$, and

$$\xi(t) \equiv \langle \Psi_0 | e^{-i\hat{H}t/\hbar} | \Psi_0 \rangle = \langle \Psi_0 | \Psi_t \rangle, \quad (2.2)$$

where Ψ_0 is the initial ground state wavefunction multiplied by the transition dipole moment.

In terms of the Feynman kernel $K_t(\mathbf{q}', \mathbf{q})$,

$$K_t(\mathbf{q}', \mathbf{q}) \equiv \langle \mathbf{q}' | e^{-i\hat{H}t/\hbar} | \mathbf{q} \rangle, \quad (2.3)$$

the time-evolved wavefunction Ψ_t can be expressed as

$$\Psi_t(\mathbf{q}') = \int d\mathbf{q} K_t(\mathbf{q}', \mathbf{q}) \Psi_0(\mathbf{q}), \quad (2.4)$$

where \mathbf{q} denotes the N coordinates of the nuclear and electronic degrees of freedom (*vide infra*), and within our semiclassical model $K_t(\mathbf{q}', \mathbf{q})$ is approximated by the HK SC-IVR,^{55,58}

$$\begin{aligned} K_t^{HC}(\mathbf{q}', \mathbf{q}) &= \left(\frac{1}{2\pi\hbar} \right)^N \int_{-\infty}^{\infty} d\mathbf{p}_0 \int_{-\infty}^{\infty} d\mathbf{q}_0 \\ &\times C_t(\mathbf{p}_0, \mathbf{q}_0) g_{\mathbf{q}', \mathbf{p}_t}(\mathbf{q}') \\ &\times \exp \left[\frac{i}{\hbar} S_t(\mathbf{p}_0, \mathbf{q}_0) \right] g_{\mathbf{q}_0, \mathbf{p}_0}(\mathbf{q})^*. \end{aligned} \quad (2.5)$$

The integration variables $(\mathbf{p}_0, \mathbf{q}_0)$ in Eq. (2.5) are the initial conditions for classical trajectories, $\mathbf{q}_t \equiv \mathbf{q}_t(\mathbf{p}_0, \mathbf{q}_0)$ and $\mathbf{p}_t \equiv \mathbf{p}_t(\mathbf{p}_0, \mathbf{q}_0)$ are the time-evolved coordinates and momenta, and $S_t(\mathbf{p}_0, \mathbf{q}_0)$ the classical action along this trajectory, obtained by integrating the following equation:

$$\frac{dS_t}{dt} = \mathbf{p}_t \cdot \dot{\mathbf{q}}_t - H(\mathbf{p}_t, \mathbf{q}_t), \quad (2.6)$$

along with the usual classical equations of motion.

The functions $g_{\mathbf{q}', \mathbf{p}_t}(\mathbf{q})$ are Gaussian wavepackets (minimum uncertainty wavepackets or coherent states),

$$\begin{aligned} g_{\mathbf{q}', \mathbf{p}_t}(\mathbf{q}) &= \prod_{j=1}^N \left(\frac{2\gamma(j)}{\pi} \right)^{1/4} \exp \left(-\gamma(j) [q(j) - q_t(j)]^2 \right. \\ &\left. + \frac{i}{\hbar} p_t(j) [q(j) - q_t(j)] \right). \end{aligned} \quad (2.7)$$

The Hamiltonian $H(\mathbf{p}_t, \mathbf{q}_t)$ in Eq. (2.6) above is the Meyer–Miller classical analog Hamiltonian for nuclear and electronic degrees of freedom,

$$\begin{aligned} H(\mathbf{R}, \mathbf{P}, \tilde{\mathbf{p}}, \mathbf{x}) &= \frac{\mathbf{P}^2}{2m} + \frac{1}{2} \sum_k \sum_{k'} [\tilde{p}(k) \tilde{p}(k') \\ &+ x(k)x(k')] H_{k,k'}(\mathbf{R}) - \frac{1}{2} \sum_k H_{k,k}(\mathbf{R}), \end{aligned} \quad (2.8)$$

where (\mathbf{R}, \mathbf{P}) and $(\mathbf{x}, \tilde{\mathbf{p}})$ denote the nuclear and electronic coordinates and momenta, respectively [$\mathbf{q} \equiv (\mathbf{R}, \mathbf{x})$ and $\mathbf{p} \equiv (\mathbf{P}, \tilde{\mathbf{p}})$ denote the nuclear and electronic variables collectively]. The first term in Eq. (2.8) is the nuclear kinetic energy and the diabatic electronic Hamiltonian matrix elements, $H_{k,k'}(\mathbf{R})$, are assumed to be real and symmetric.

Finally, the preexponential factor in the integrand of Eq. (2.5) is given by

$$C_t(\mathbf{p}_0, \mathbf{q}_0) = \sqrt{\det[\mathbf{M}]}, \quad (2.9)$$

where \mathbf{M} is a linear combination of components of the monodromy matrix,

$$\begin{aligned} M(j, k) &= \frac{1}{2} \left(\frac{\partial q_t(k)}{\partial q_0(j)} + \frac{\gamma(j)}{\gamma(k)} \frac{\partial p_t(k)}{\partial p_0(j)} - \frac{1}{2i\hbar} \frac{\partial p_t(k)}{\partial q_0(j)} \right. \\ &\left. - 2i\hbar \gamma(j) \frac{\partial q_t(k)}{\partial p_0(j)} \right), \end{aligned} \quad (2.10)$$

where $\gamma(j)$ are the constant parameters in the Gaussian wavepackets of Eq. (2.7). The various time dependent partial derivatives are obtained by numerical integration of the following equations for the stability matrix:

$$\begin{aligned} \frac{d}{dt} \left(\frac{\partial p_t(i)}{\partial z(j)} \right) &= - \sum_{k=1}^N \left(\frac{\partial^2 H(\mathbf{p}_t, \mathbf{q}_t)}{\partial p_t(k) \partial q_t(i)} \frac{\partial p_t(k)}{\partial z(j)} \right. \\ &\left. + \frac{\partial^2 H(\mathbf{p}_t, \mathbf{q}_t)}{\partial q_t(k) \partial q_t(i)} \frac{\partial q_t(k)}{\partial z(j)} \right), \\ \frac{d}{dt} \left(\frac{\partial q_t(i)}{\partial z(j)} \right) &= + \sum_{k=1}^N \left(\frac{\partial^2 H(\mathbf{p}_t, \mathbf{q}_t)}{\partial p_t(k) \partial p_t(i)} \frac{\partial p_t(k)}{\partial z(j)} \right. \\ &\left. + \frac{\partial^2 H(\mathbf{p}_t, \mathbf{q}_t)}{\partial q_t(k) \partial p_t(i)} \frac{\partial q_t(k)}{\partial z(j)} \right), \end{aligned}$$

where $z = p_0$ or q_0 .

As presented above, the computational task is to evaluate a rather high dimensional phase space average over initial conditions defined as follows:

$$\begin{aligned} \xi(t) &= \left(\frac{1}{2\pi\hbar} \right)^N \int_{-\infty}^{\infty} d\mathbf{p}_0 \int_{-\infty}^{\infty} d\mathbf{q}_0 C_t(\mathbf{p}_0, \mathbf{q}_0) \\ &\times \exp \left[\frac{i}{\hbar} S_t(\mathbf{p}_0, \mathbf{q}_0) \right] \Psi^{s*}(\mathbf{q}', \mathbf{p}_t) \Psi^s(\mathbf{q}_0, \mathbf{p}_0), \end{aligned} \quad (2.11)$$

where $\Psi^s(\mathbf{q}, \mathbf{p})$ is the coherent state transform of the initial wave function,

$$\Psi^s(\mathbf{q}, \mathbf{p}) = \int d\mathbf{q}' g_{\mathbf{p}, \mathbf{q}}(\mathbf{q}')^* \Psi_0(\mathbf{q}'). \quad (2.12)$$

In order to damp out the most oscillatory regions of the integrand (which make little contribution to the value of the integral), we have utilized a simplified version of the

Filinov,^{93,40} or stationary phase Monte Carlo (SPMC) method.⁹⁴ Specifically, the integral for $\xi(t)$ has the form

$$\xi(t) = \int_{-\infty}^{\infty} d\mathbf{z} A(\mathbf{z}) \exp\left[\frac{i}{\hbar} \varphi(\mathbf{z})\right], \quad (2.13)$$

where \mathbf{z} is a $2N$ integration variable defining the initial coordinates and momenta, while A and φ are real. Keeping only the linear part of the Filinov transformation has the effect of inserting a convergence factor into the integrand of Eq. (2.13), which is the exponential of the square gradient of the phase, i.e.,

$$\xi(t) = \int_{-\infty}^{\infty} d\mathbf{z} A(\mathbf{z}) \exp\left\{\frac{i}{\hbar} \varphi(\mathbf{z}) - \frac{1}{2\hbar\beta} [\nabla \varphi(\mathbf{z})]^2\right\}. \quad (2.14)$$

This clearly has the effect of weighting regions of the integrand where the phase is most slowly varying. Though the more general Filinov/SPMC expressions,^{93,40,94} which involve second derivatives of the phase, are presumably more accurate, they are more difficult to use. This simplified linear version, with $\beta = 20\,000$ a.u., has proved to be quite adequate for our present application and has also been tested by Herman for the two dimensional Henon–Heiles model system with satisfactory results.⁵²

B. Sample preparation and photoexcitation

In our simulations trajectories are initialized through MC sampling of coordinates and momenta according to localized phase space distributions that match the excited state populations created under the assumption that the photolysis event promotes molecules instantaneously from the ground electronic state, X , to the optically allowed excited states which are resonant with the excitation energy [Franck–Condon (FC) approximation].

With regard to the optically allowed excited states that are populated by photoexcitation and participate in the dynamics of relaxation, we assumed that the most important electronic states in the Chappuis system are the two lower lying excited states of ${}^1A''$ symmetry ($1\,{}^1A''$ and $2\,{}^1A''$, with 1A_2 and 1B_1 electronic symmetry, respectively, in C_{2v}). This assumption is based on considerations of the absorption bands of ozone³ together with the results of *ab initio* calculations.^{5,10,11,16–19} In addition to the ground electronic state information, we therefore include in our simulations the two diabatic PESs, V_1 and V_2 , that correspond to the excited states of ${}^1A''$ symmetry mentioned above, the coupling potential $V_{1,2}$ between these two electronic states, and the transition dipole moments from these two excited state PESs to the ground state. These five quantities ($V_1, V_2, V_{1,2}, \mu_1, \mu_2$), have been calculated by Woywod *et al.*¹⁶ as functions of the two OO bond distances ($1.8 \text{ a.u.} \leq R_1, R_2 \leq 3.55 \text{ a.u.}$) and the $O\hat{O}O$ bending angle ($0 \leq \alpha \leq \pi$), using the CASPT2 *ab initio* method. In our simulations we calculate the values of these quantities at arbitrary points within the limits of the grids using a spline interpolation subroutine.⁹⁵ Our simulations, thus model nonadiabatic dynamics on full *ab initio* PESs without relying on any approximate model potential.

The nuclear wave function that represents the initial population in the X state is assumed to be its ground vibrational wave function,

$$\Psi_{gr}(\mathbf{R}) = \prod_{j=1}^3 \left(\frac{\alpha_j}{\pi}\right)^{1/4} \exp\left(-\frac{\alpha_j}{2} R(j)^2\right), \quad (2.15)$$

where $R(j)$ represents the j th normal mode coordinate of the molecule in its electronic ground state and $\alpha_j = \sqrt{k_j \mu / \hbar^2}$, where k_j is the harmonic constant of such normal mode and μ represents the mass of an oxygen atom. The equilibrium values for bond lengths and bending angle are set equal to the values employed in full quantum calculations by Schinke and co-workers: $R_1 = R_2 = 2.46$ a.u. and $\alpha = 116.8^\circ$, which are just slightly different from the equilibrium values ($R_1 = R_2 = 2.403$ a.u. and $\alpha = 116.78^\circ$) from Ref. 96. This initial wave function is constructed on the basis of the low temperature approximation, i.e., assuming that contributions from anharmonicity and higher vibrational levels can be neglected, since measured experimental cross sections vary only slightly with temperature, $< 1\%$, between 550 and 660 nm in the 220–280 K range of temperatures.⁹⁷ However, at wavelengths away from the peak we expect our assumption to be an oversimplifying approximation since the absorption cross sections decrease with decreasing temperature, e.g., $\sim 40\%$ at 420 nm between 298 and 220 K.⁹⁷

Unfortunately, the ground state PES has not been calculated at the same level of theory, so the harmonic frequencies $\omega_j = \sqrt{k_j / \mu}$ for the symmetric, asymmetric and bending modes of the molecule are taken from the ground state potential energy surface of Ref. 96. This combination of PESs from different sources introduces some uncertainty in the coordinates of the FC point, as well as in the initial populations of the optically allowed excited states that are determined by the dipole moments of transition and the relative positions of the ground and excited state PESs.

The total wave function for the initial state of the system is the product of electronic and nuclear wave functions,

$$\Psi_{0,k}(\mathbf{x}, \mathbf{R}) = \sqrt{\frac{2}{\pi}} x_k \exp\left[-\frac{1}{2}(x_1^2 + x_2^2)\right] \mu_k \Psi_{gr}(\mathbf{R}), \quad (2.16)$$

where $\Psi_{gr}(\mathbf{R})$ is defined by Eq. (2.15) and k denotes the initial electronic state. The electronic wave function in Eq. (2.16) is a product of one dimensional harmonic oscillator wave functions, since these are the eigenfunctions of the part of the quantum Hamiltonian that models the electronic degrees of freedom [cf. Eq. (2.8)]. The electronic wave function for state k is a ground state harmonic oscillator wave function for all electronic modes except the k th one, which has one quantum of excitation. Finally, the total autocorrelation function is given by

$$\xi(t) = \langle \Psi_{0,1} | \Psi_{t,1} \rangle + \langle \Psi_{0,2} | \Psi_{t,2} \rangle, \quad (2.17)$$

where most of the contribution to the autocorrelation function comes from the second term of the right-hand side of Eq. (2.17), since the transition moment to state 2 is symmet-

ric in the FC region and much larger than the transition dipole moment to state 1 which is antisymmetric, and therefore equal to zero in C_{2v} .

III. RESULTS

We present our results in two sections. First, Sec. III A presents the comparison of our calculated absorption spectrum with both the spectrum from full quantum calculations by Schinke and co-workers,⁹⁸ and the experimental absorption band for the Chappuis system.^{7,8} In Sec. III A we also present a comparison of the autocorrelation function $\xi(t)$ obtained via our semiclassical methodology of Sec. II and the corresponding results from full quantum calculations.⁹⁸ After demonstrating the accuracy of our calculations, we present in Sec. III B an analysis of the phase space dynamics of nuclear and electronic variables for a small ensemble of trajectories and demonstrate the relative importance of the various phase space dynamical variables in the spectroscopic features presented in Sec. III A. The connection between the quantum dynamics of the system in Hilbert space and the classical dynamics of representative trajectories in phase space is intended to provide an intuitive understanding of the more fundamental aspects of photodissociation reaction dynamics of a small polyatomic system, and results from the fact that the various intensities of absorption are determined by the time dependent overlap of Ψ_t and Ψ_0 which is ultimately controlled by the semiclassical phase space dynamics of nuclear and electronic variables components during the photolysis event. Namely, the motion of the system in Hilbert space results from the interferences of the constituent wave packets. The resulting time dependent interference phenomena responsible for relaxation of population, dephasing and recurrence take place within our formalism on the basis of the overlap of the constituent localized wave packets that evolve in phase space according to classical equations of motion.

According to the semiclassical methodology presented in Sec. II, the evaluation of the autocorrelation function $\xi(t)$ for the system of three normal coordinates evolving on two electronic surfaces coupled by a conical intersection involves the computation of a 10 dimensional integral with an oscillatory integrand, for which it is necessary to propagate 111 variables that include nuclear and electronic coordinates and momenta, the partial derivatives of each of them with respect to the initial coordinates and momenta, and the classical action. Since most of the degrees of freedom involved in the equations of motion are rapidly changing variables, it is necessary to employ a fairly small integration step $\delta=0.003$ fs in order for the equations of motion to be integrated accurately, and to re-initialize the stability matrix every 0.25 fs and calculate the partial derivatives at longer times according to the chain rule. The values of the parameters $\gamma(j)$ for the electronic degrees of freedom j are arbitrarily set equal to 1 a.u., while $\gamma(j)$ for the nuclear variables are a set equal to $\alpha(j)$ which are introduced by Eq. (2.15). All forces and second derivatives necessary for integrating the equations of motion presented in Sec. II B are calculated using finite difference ex-

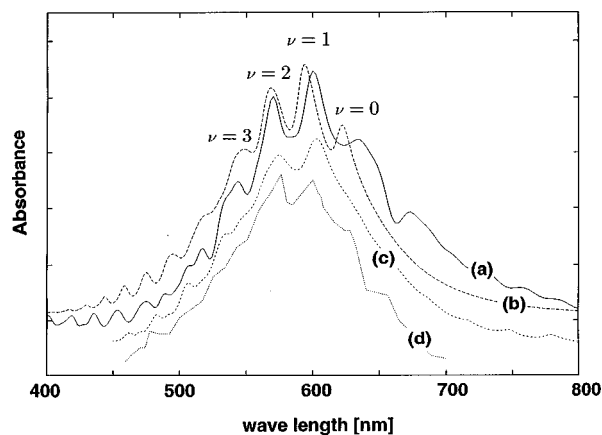


FIG. 1. Comparison of our calculated absorption spectrum for O_3 for the visible region as described in Sec. II [solid curve (a)], with the corresponding full quantum results (Ref. 98) [short dashes (b)], the gas phase absorption spectrum of $^{16}O_3$ at 298 K and 40 Torr by Anderson *et al.* (Ref. 7) [dots (c)] and the absorption spectra for the Chappuis system (Ref. 8) of O_3 dissolved in O_2 at 77 K [long dashes (d)]. Calculated spectra [curves (a) and (b)] are artificially shifted by 14 nm (50 meV) to longer wavelengths in order to facilitate the comparison. The diffuse vibrational structures are assigned according to Ref. 7 to transient vibrational excitation of the symmetric stretch mode with quantum numbers $\nu=0,1,2,\dots$. All the curves in this figure, have also been vertically shifted to facilitate the comparison.

pressions, and the configurational space is restricted within the limits of the spatial grid as described in Sec. II B. Trajectories that crossed the boundaries of the grid are terminated and their contributions to the autocorrelation function set to zero at all later times. This approximate procedure implicitly assumes that trajectories that go beyond the boundaries of the grid do not return to the reaction center at later times, and is a good approximation for our system since in the gas phase there is no surrounding environment that could reflect the dissociation fragments back to the reaction center. We also checked this approximation by performing calculations on PESs that were extended to a wider configurational space and obtained identical results.

The calculations of the autocorrelation function are converged with 100 000 trajectories that are calculated with a programming model to perform semiclassical dynamics in a portable single program multiple data (SPMD) streams code that runs under the message passing interface (MPI) environment and is optimized for nodes that are relatively powerful. At the hardware level, we thus have coarse-grained parallelism, allowing us to allocate hundreds or thousands of trajectories per node, minimizing communication costs on the parallel architecture.

A. Comparison of semiclassical results with experiments and full quantum calculations

In Fig. 1 we present the comparison of our calculated absorption cross section for O_3 as a function of photon wavelength [solid line (a)] with the corresponding experimental⁷ absorption spectrum at room temperature [dots (c)], and the spectrum obtained from full quantum calculations by Schinke and co-workers⁹⁸ [short dashes (b)]. The semiclassical and full quantum calculated spectra are

shifted about 14 nm to longer wavelengths to facilitate the comparison with experiments. This small shift of about 50 meV to smaller photon energies indicates the accuracy of the *ab initio* PESs and allows us to center the overall calculated bands with the experimental signals.

The first feature to note in comparing our calculated spectrum with the experimental results is that the overall qualitative features of the experimental data are well reproduced by our calculations in terms of the overall shape, as well as the spacing and the widths of the diffuse structures superimposed on the broad background. However, in addition to the small shift in the position of the band noted above, there are also some differences in the superimposed structure of resonances that is more pronounced in the calculated semiclassical and full-quantum absorption cross sections than in the experimental data. There is also a small difference in the spacing of the diffuse structure in the full quantum calculation compared to that in the semiclassical result. The origin of this can be traced to the recurrence feature in the survival amplitude (or autocorrelation function), which appears at ~ 30 – 40 fs in the semiclassical calculation but not until ~ 40 – 50 fs in the full quantum result. The SC-IVR spectrum also shows some presumably artificial structure in the low frequency tail, which is due to the small peaks in the autocorrelation at times between 40 and 60 fs.

The physics involved in the dynamics of relaxation responsible for these general spectroscopic features observed in this spectrum is addressed in Sec. III B in terms of the analysis of the phase space dynamics of semiclassical trajectories, where we show that the photolysis event predominantly populates the binding $2^1A''$ excited state where the molecule performs essentially symmetric stretch motion at very short times, and couples to the dissociative state which depletes the bound state through the antisymmetric mode and leads to fragmentation into an $O_2(^3\Sigma_g^-)$ molecule and an $O(^3P)$ atom. Thus, the origin of the structure is the transient excitation of the symmetric stretch motion on the bound excited state PES assigned according to Ref. 7 with quantum numbers $\nu=0$ (peak at about 640 nm), $\nu=1$ (peak at 600 nm), $\nu=2$ (peak at about 565 nm), $\nu=3$ (peak at about 535 nm), $\nu=4$ (peak at about 510 nm), etc. This bound motion is damped by nonadiabatic transitions to the dissociative state which is responsible for the diffuse character of the absorption band, whereas the bending motion does not participate in any relevant aspect of the dynamics of relaxation. This interpretation points to small inaccuracies of the coupling between the bound and dissociative PESs as responsible for having excited state bound motion along the symmetric stretch coordinate that is slightly more stable and recurrent than the dynamics observed experimentally. The experimental data, thus suggests a stronger coupling in order to have a relaxation of population in the bound state and to quench the $\nu=0$ band. To illustrate the effect of external dynamical perturbations on the vibronic coupling between the two surfaces, we also show in Fig. 1 [long dashes (d)] the experimental absorption spectrum of O_3 dissolved in liquid oxygen at 77 K;⁸ one sees an enhancement of the absorption cross section of weak bands ($\nu=0$ band), as well as a significant

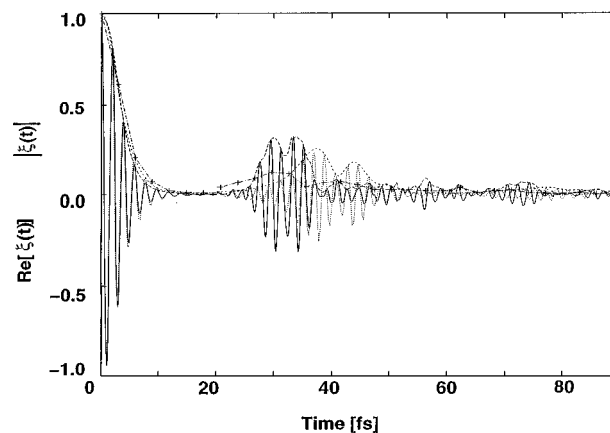


FIG. 2. Comparison of the modulus (long dashes) and real part (solid line) of the autocorrelation function $\xi(t)$ for the first 90 fs of dynamics calculated according to the semiclassical methodology presented in Sec. II, and the full quantum results obtained by Schinke and co-workers (Ref. 98) (in dots and short dashes, respectively), as well as the amplitude of the autocorrelation function derived from the $^{16}O_3$ experimental absorption spectra by Anderson *et al.* (Ref. 7) (dot-dash curve). The vertical scale has been expanded by a factor of 5 to facilitate the comparison for all times beyond 20 fs.

enhancement of the relative absorption cross section in the visible band versus the ultraviolet band.

In order to check the accuracy and reliability of our semiclassical methodology we show in Fig. 2 the comparison of the real part and the modulus of our calculated autocorrelation function $\xi(t)$ with the amplitude of the autocorrelation function derived from the $^{16}O_3$ experimental absorption spectra by Anderson *et al.*,⁷ as well as with the corresponding full-quantum results obtained by Schinke and co-workers⁹⁸ for the same initial state. With the exception of small deviations in the shape of the envelope of the autocorrelation function, one sees that the semiclassical results are in very good agreement with the experimental data as well as with the full quantum calculations throughout the whole dynamical range of ozone photodissociation, starting with an ultrafast fall-off of the overlap between the initial and final wave functions (within the first 15–20 fs of dynamics) that is caused by Ψ_t moving away from Ψ_0 as the system slides down along the reaction coordinate of the effective excited state PES. This ultrafast relaxation at very short times is responsible for the broad envelope of the absorption spectrum in the frequency domain presented in Fig. 1, and all the subsequent dynamics at longer times determines the fine structure in the frequency spectrum but does not affect the position or overall width of the absorption band. This longer time dynamics gives rise to an extra feature of the autocorrelation function at about 25–50 fs. The intensity of this recurrence feature is slightly more pronounced in the calculated full quantum and semiclassical survival amplitudes (or autocorrelation functions), compared to the experimental results. The recurrence feature in the full quantum calculations is shifted by ~ 10 fs compared to both the experimental and the semiclassical results. This recurrence feature results from the partial overlap of the initial and final wave functions caused by a partial recurrence of the final wave function Ψ_t to the region of the configurational space occupied by the

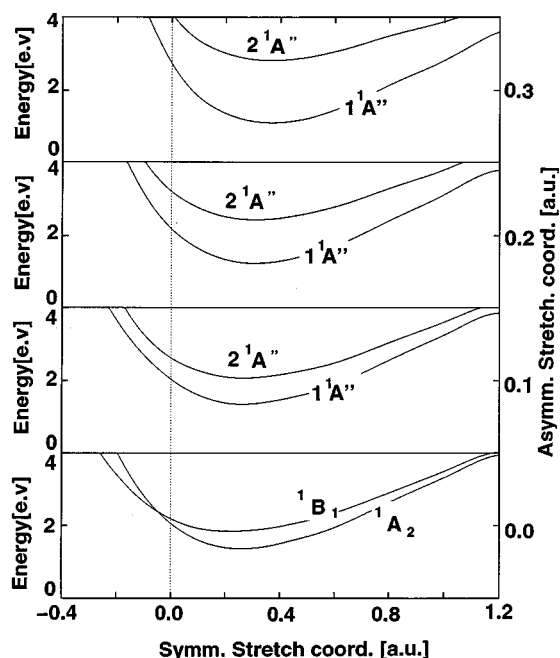


FIG. 3. Adiabatic potential energy surfaces for the $1^1A'$ and $2^1A''$ electronic states as functions of the symmetric stretch coordinate for various values of the asymmetric stretch coordinate, keeping the bending mode coordinate fixed at the origin.

initial state of the system, Ψ_0 . This qualitative description is generally applicable to other polyatomic systems^{99,100} and serves as a model of dynamics of predissociation when the PESs responsible for relaxation are coupled by a conical intersection.

B. Phase space dynamics

In this section we exploit the benefit of having a theoretical framework where both nuclear and electronic degrees of freedom are treated on the same dynamical footing and show how the various spectroscopic features of the Chappuis band of ozone presented in Sec. III A are associated with the phase space dynamics of nuclear and electronic variables. For example, the position of the absorption band is determined by the high frequency motion of the electronic variables on the PESs parametrized by nuclear coordinates, while the bandwidth and superimposed structure depends on the nuclear dynamics on the effective PES which is an average determined by the values of the electronic variables. We analyze the phase space evolution of coordinates and momenta of a small ensemble of trajectories and determine the relative importance of the different dynamical variables on each of the spectroscopic features.

In this section all normal coordinates are defined as in Sec. II B in terms of the normal modes of the molecule in the electronic ground state PES taken from Ref. 96. Figure 3 shows the $1^1A'$ and $2^1A''$ PESs along the symmetric stretch coordinate for values of the asymmetric stretch coordinate ranging from 0.0 to 0.3 a.u., with the bending coordinate held fixed at the origin. From Fig. 3 one can see that the PESs are bound along the symmetric stretch coordinate, with

equilibrium positions displaced from the origin and located at about 0.2–0.4 a.u., for all values of the asymmetric stretch coordinate. This specific topology of the excited state PESs, where the equilibrium geometry along the symmetric stretch coordinate is displaced outward from the FC region, causes the semiclassical trajectories to be immediately displaced after photoexcitation from their initial symmetric distribution toward the region of positive symmetric stretch coordinates and momenta. From the lower set of curves of Fig. 3 (asymmetric stretch coordinate equal to 0.0 a.u.), it is also expected that trajectories moving outbound along the symmetric stretch coordinate, which have small coupling with the asymmetric mode, will have very small vibronic coupling between the two excited state PESs (as it can be observed from the crossing point of the two surfaces) and will undergo almost unperturbed motion until they encounter the repulsive wall of the outer turning point at beyond 0.4 a.u. Under these circumstances the dispersion in the coordinates of the turning points will be determined by the initial distribution of symmetric stretch coordinates and momenta. On the other hand, semiclassical trajectories evolving away from C_{2v} symmetry (upper three panels of Fig. 3) will have significant contributions of the asymmetric mode coupled to the symmetric stretch motion, and consequently the turning points along the symmetric stretch coordinate will be dispersed by the different possible values of the asymmetric stretch coordinate. Furthermore, these trajectories will also have significant electronic coupling (as it can be observed from the increasing gap separating the two PESs) that will cause further dispersion corresponding to all the possible values of the average PES determined by the electronic variables. All these features of the early time dynamics can be observed in Fig. 4 where we show the first 90 fs of dynamics after photoexcitation of the sample for an ensemble of 50 representative trajectories. Panel (a) shows the time evolution and panel (b) the phase space dynamics along the symmetric stretch coordinate, along with the initial ensemble distribution (scattered points). From panel (a) one sees that during the first 10 fs of dynamics the ensemble of trajectories that is initially symmetrically distributed around the origin of coordinates is displaced so that all trajectories obtain positive values of the symmetric stretch coordinate, and at about 15–25 fs all trajectories reach their farthestmost distance from the origin along the symmetric stretch coordinate. Thus, the overlap of Ψ_t with Ψ_0 is minimum at this time, as seen in Fig. 2. It can also be observed from panel (a) of Fig. 4 that turning points for the first extension of the molecule along the symmetric stretch coordinate are widely dispersed over about 0.6 a.u., in accord with the discussion presented above where the origin of this dispersion is explained from the topology of the excited state PESs, the initial phase space distribution, the coupling with the asymmetric mode, and the resulting electronic coupling between the diabatic excited state PESs involved in the process of relaxation. The phase space evolution of trajectories displayed in panel (b) of Fig. 4 shows that the motion along the symmetric stretch coordinate is periodic, which indicates that the overlap of Ψ_t with Ψ_0 is expected to increase at longer times from its minimum value at 15–20 fs

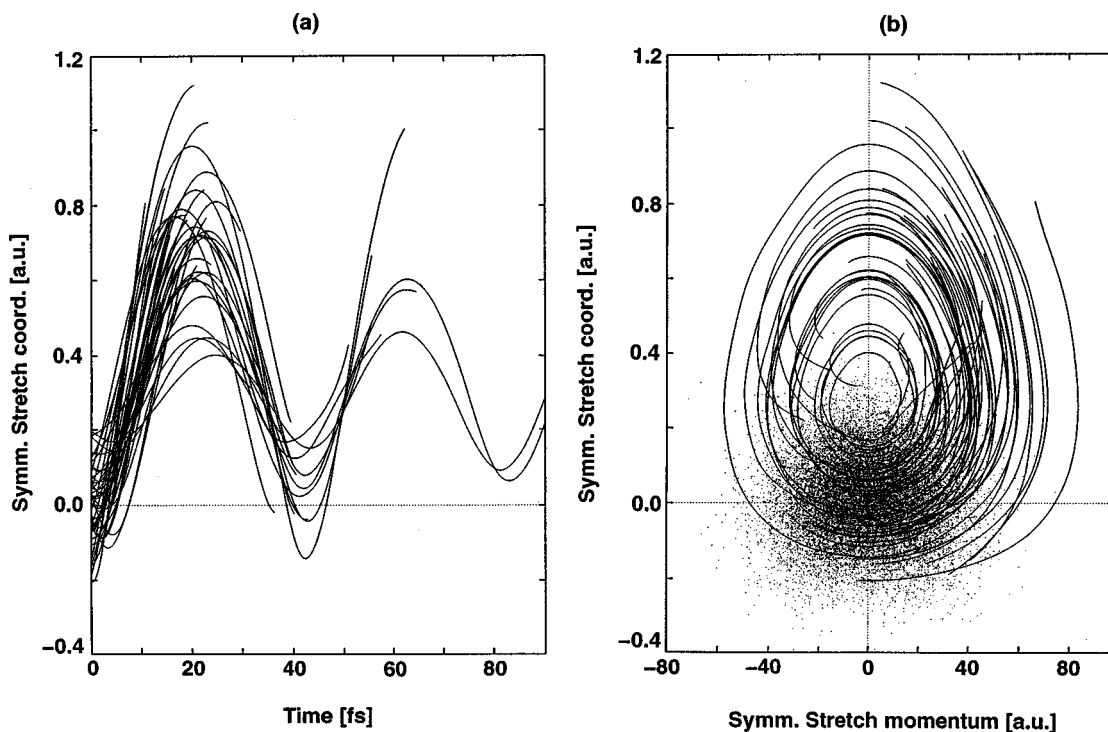


FIG. 4. Panel (a) shows the time evolution of the symmetric stretch coordinates of an ensemble of 50 representative trajectories. Panel (b) shows the phase space dynamics projected onto the plane defined by the symmetric stretch coordinates and momenta for the same ensemble of trajectories and the initial ensemble distribution (scattered points).

as trajectories return to the proximity of the region of initial coordinates at about 30–50 fs. This results in the recurrence feature of the autocorrelation function at about 30–50 fs, as seen in Fig. 2. It is also interesting to note from Fig. 2 that this recurrence feature of the autocorrelation function has a superimposed structure that can be clearly understood in terms of the phase space dynamics of the recurrent trajectories, as popularized by Heller⁵⁴ in the context of semiclassical dynamics. From panel (a) of Fig. 4 it is evident that this superimposed structure arises from the interferences of the contributions of recurrent trajectories that return to the FC region dephased with respect to each other. The origin of this dephasing among recurrent trajectories is mostly determined by the initial distribution of momenta, which makes trajectories with initial negative momentum along the symmetric stretch coordinate to be delayed relative to those with initial positive momentum, since it takes some time for those with negative momentum to reach the inner turning point and invert their direction of motion. Furthermore, trajectories with different initial coordinates are expected to be slightly dephased with respect to each other due to the anharmonicity of the average PES along the symmetric stretch coordinate. The spectral consequence of the interferences among recurrent trajectories that are slightly dephased with respect to each other is reflected in the shape of the resonances in Fig. 1 that are not sharp and well defined, but rather diffuse and with spacings that change throughout the spectrum.

Another important aspect that can be observed from Fig. 4 and that is associated with the recurrence feature of the autocorrelation function is that only a few of the total num-

ber of trajectories have uninterrupted orbits and return completely to the proximity of the FC point at about 30–50 fs. Thus, the overlap of Ψ_t with Ψ_0 will be much smaller than the initial overlap, and each successive recurrence event [such as recurrences at about 80–90 fs from panel (a) of Fig. 4] will have an even smaller overlap amplitude, since it will be invariably associated with a smaller number of uninterrupted trajectories. In order to understand the origin of these interruptions observed along the motion of the symmetric mode, we show in panel (a) of Fig. 5 the time evolution of the ensemble of trajectories along the asymmetric stretch coordinate and in panel (b) the corresponding phase space dynamics and initial distribution. The trajectories in panel (a) clearly show that the motion along the asymmetric stretch coordinate is rather unstable and responsible for dissociation of the O_3 molecule into an $O_2(^3\Sigma_g^-)$ molecule and an $O(^3P)$ atom, diminishing the number of trajectories in the vicinity of the FC region at longer times. The dissociative character of the asymmetric mode is also evident from the phase space dynamics presented in panel (b) showing that dissociative trajectories in general have large values of momentum along the asymmetric stretch coordinate. However, it is also evident from Fig. 5 that the average PES along the asymmetric stretch coordinate is not simply dissociative, since during the first 10 fs of dynamics the amplitudes of the asymmetric stretch motion usually decrease and trajectories undergo a quasiperiodic motion along this coordinate before becoming unstable. At this point, it is of interest to investigate whether the dissociative character of the asymmetric stretch motion is

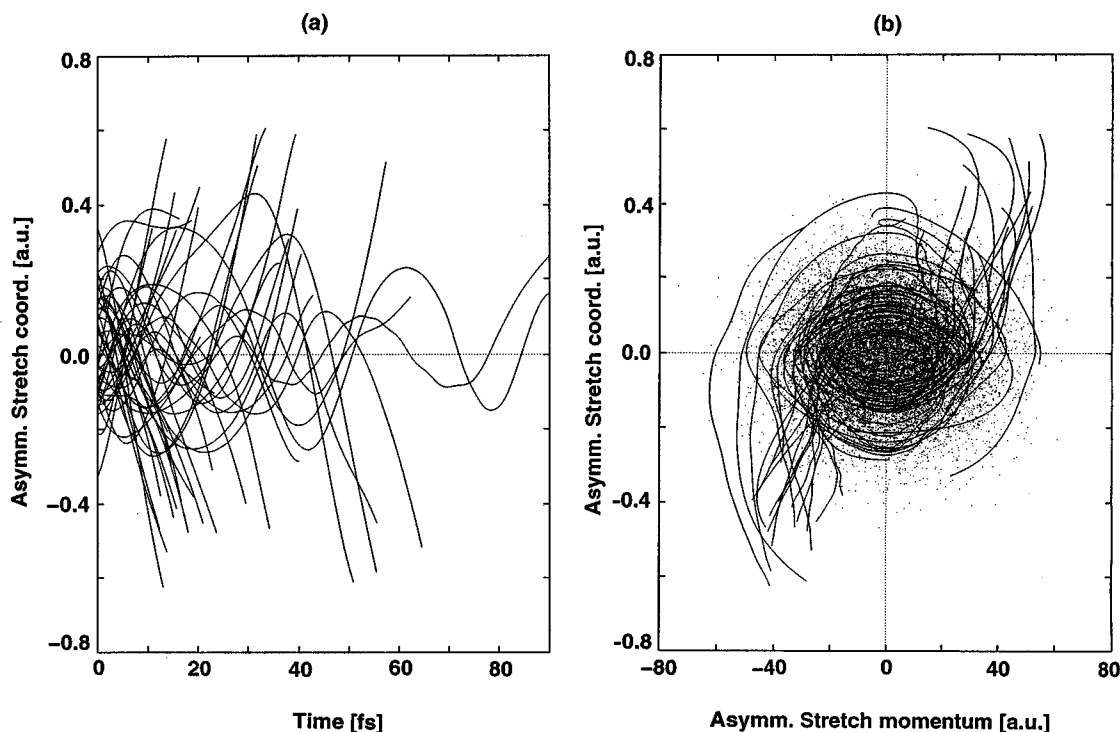


FIG. 5. Panel (a) shows the time evolution of the asymmetric stretch coordinates for the same ensemble of 50 representative trajectories as presented in Fig. 4. Panel (b) shows the phase space dynamics projected onto the plane defined by the asymmetric stretch coordinate and momentum and the initial ensemble distribution (scattered points).

actually being turned on by the dynamics of the other nuclear and electronic coordinates of the system. In order to address this issue, we show in Fig. 6 the adiabatic PESs as functions of the asymmetric stretch coordinate for values of the sym-

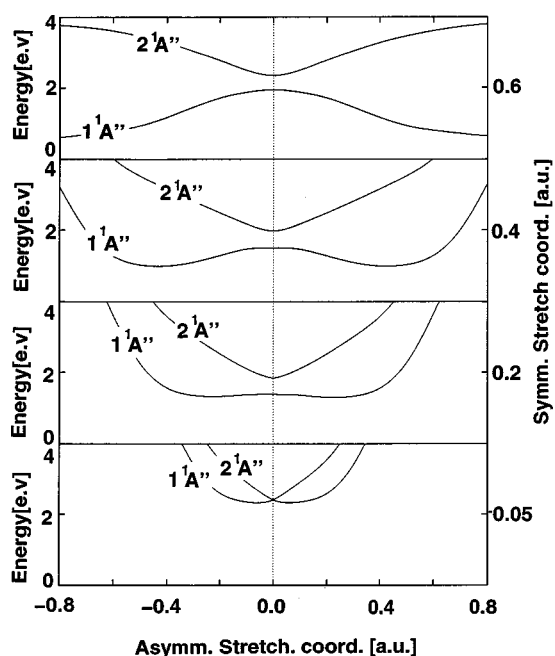


FIG. 6. Adiabatic potential energy surfaces for the $1^1A'$ and $2^1A''$ electronic excited states as functions of the asymmetric stretch coordinate for various values of the symmetric stretch coordinate, keeping the bending mode coordinate fixed at the origin.

metric stretch coordinate ranging from -0.05 to 0.6 a.u. The first important observation from Fig. 6 is that the PES of the $2^1A''$ state, which is the most optically active of the two electronic excited states, is actually bound along the asymmetric stretch coordinate throughout the range of values of the symmetric stretch coordinate presented in Fig. 6 and with its equilibrium position always located at the origin. Thus, it is reasonable to expect that so long as the average PES has a predominant contribution from the $2^1A''$ state, trajectories will exhibit bound motion along the asymmetric stretch coordinate and on each oscillation pass the origin of coordinates with maximum speed.

On the other hand, the topology of the $1^1A''$ state is completely different from the PES of the $2^1A''$ state along the asymmetric stretch coordinate, since for fixed values of the symmetric stretch coordinate it has the shape of a double well with a barrier at the origin (which determines the point of maximum proximity between the two excited state PESs), and equilibrium positions that lead to dissociation of the molecule that are symmetrically located on both sides of the barrier, progressively farther away from the origin and further stabilized as the molecule is extended along the symmetric stretch coordinate. Thus, as soon as the electronic variables introduce dominant contributions from the lower $1^1A''$ excited state, the average curvature along the asymmetric stretch coordinate becomes negative. This average is determined by the values of the electronic variables, which define the relative probability of being on each of the two excited states, as well as by the values of the curvatures along the asymmetric stretch coordinate of these excited state PESs

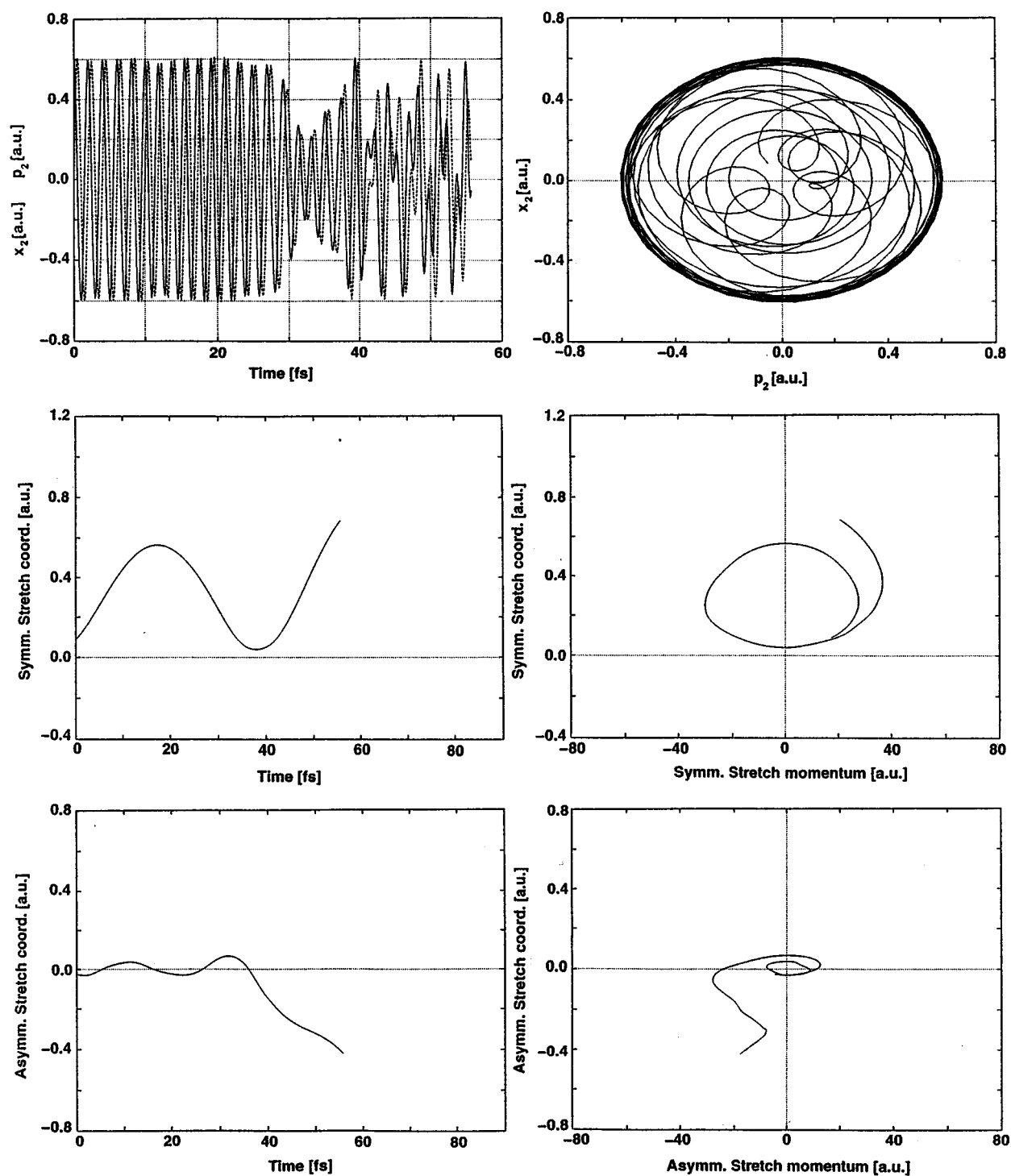


FIG. 8. Phase space dynamics of electronic and nuclear degrees of freedom for a single representative trajectory. Panels in the first row show a typical trajectory for the electronic coordinate associated with diabatic state $2^1A'$ as a function of time and the corresponding dynamics in the electronic phase space. Second and third rows of this figure show the evolution of the symmetric stretch and asymmetric stretch coordinates respectively as functions of time for the same trajectory and the corresponding phase space diagrams.

30–40 fs, the average PES becomes an admixture of the two excited state PESs. The nonlinear terms introduced in the equations of motion by the electronic coupling makes the electronic motion no longer periodic as can be observed in the first row of Fig. 8, and the asymmetric stretch motion becomes unstable through coupling to the dynamics of the

symmetric stretch coordinate (lower two panels of Fig. 8). Consequently, the molecule dissociates.

IV. CONCLUSIONS

In this paper we have demonstrated the capabilities of the Meyer–Miller classical model for nuclear and electronic

dynamics quantized according to the HK SC-IVR methodology, together with stationary phase MC methods, by simulation of the nonadiabatic relaxation dynamics associated with the Chappuis band of ozone following photoexcitation of the molecule in the gas phase with visible light. While our computational method is still in its early stages of development for general purpose applications that might involve longer time dynamics and systems with more nuclear and electronic degrees of freedom, this first application to studies of ozone visible photodissociation has allowed explicit calculation of the most relevant quantities that characterize the electronic and nuclear relaxation dynamics during the photolysis event, and provided an intuitive interpretation of the absorption spectra in the frequency domain in terms of the analysis of the phase space dynamics of representative semiclassical trajectories. This at least demonstrates the potentiality of this methodology for studying reactions involving nonadiabatic complex quantum dynamics in polyatomic systems. In the spirit of the original formulation of Meyer and Miller, the method treats nuclear and electronic degrees of freedom on the same dynamical footing and involves the propagation of deterministic classical trajectories on an average PES. Here, however, the dynamics is treated within the semiclassical IVR model rather than the more primitive quasiclassical model used earlier. Interference (i.e., quantum coherence) and even tunneling to some extent, are thus incorporated within this description, and any quenching of interference structure comes about naturally (via destructive interference) and no *ad hoc* dephasing approximation needs to be introduced. The classical description also allows for an intuitive understanding of complex quantum dynamics associated with these nonadiabatic processes.

The agreement of our results for the autocorrelation function and absorption cross sections with the corresponding results obtained from full quantum calculations and the experimental data for the absorption spectra supports: (1) our interpretation of the experimental data in the frequency domain in terms of the transient excitation of the symmetric stretch motion on the bound excited state PES, which is damped by nonadiabatic dynamics onto the dissociative state responsible for the diffuse character of the absorption band, and (2) the relative importance of the different dynamical variables of our model on each of the spectroscopic features of the Chappuis band of ozone. However, there are also some noticeable differences between the calculated and experimental spectra that include: (1) a small shift of 50 meV in the position of the band, and (2) a structure of resonances superimposed to the broad background that is more pronounced in our calculated spectrum than in the experimental data, suggesting small inaccuracies of the coupling between the bound and the dissociative PESs.

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