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LETTER TO THE EDITOR

Periodic orbits and molecular photoabsorption

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Abstract. A method for the semiclassical evaluation of molecular photoabsorption rates in terms of contributions of periodic orbits is developed and applied to a collinear model of CO₂. It is shown that for a satisfactory quantitative description effects have to be taken into account which originate from a finite extension of the Franck–Condon transition region in comparison with the extension of Fresnel zones of the contributing periodic orbits.

The connection between photoabsorption and the classical dynamics of nuclear degrees of freedom on excited electronic potential surfaces is a problem of molecular physics of much current interest in particular in cases in which the classical dynamics is not integrable (Heller 1978, 1981, Schinke and Engel 1990, Kulander *et al* 1991). With the help of semiclassical methods Eckhardt *et al* (1992) have recently established a quantitative connection between (unstable) classical periodic orbits and semiclassical matrix elements. However, the application of their approach to the description of molecular photoabsorption processes is restricted to cases in which the extension of the Franck–Condon transition region in phase space is much larger than the Fresnel zones (Kravtsov and Orlov 1990) of periodic orbits which contribute to the photoabsorption rate. The extension of such a Fresnel zone is determined by the transverse region in phase space around a periodic orbit within which trajectories interfere constructively and thus the corresponding classical actions change at most by an amount of the order of \hbar .

Here we report results on the quantitative connection between the classical dynamics of periodic orbits on an excited electronic potential surface and photoabsorption of the CO₂ molecule within the framework of a collinear model (Kulander and Light 1980). It is shown that this rate can be calculated semiclassically from a knowledge of classical properties of four classes of periodic orbits on the excited electronic potential surface. However, good quantitative agreement between a semiclassical periodic-orbit approach and the exact quantum mechanical results is obtained only if the previously derived results of Eckhardt *et al* (1992) are generalized and effects originating from the finite extension of the Franck–Condon transition region in comparison with the Fresnel zones of the contributing periodic orbits are taken into account.

In the Franck–Condon approximation the rate for molecular one-photon absorption from an initially prepared vibrational state $|g\rangle$ with energy ϵ_g to vibrational states on an excited electronic potential surface by a weak and long laser pulse with electric field strength $E = \mathcal{E}e^{-i\omega t} + \text{cc}$ is given by

$$\Gamma(\omega) = -\frac{2|\mathcal{E}C|^2}{\hbar} \text{Im}\{(2\pi\hbar)^D \int d^D x d^D p A(x, p) G_\epsilon(x, p)\}. \quad (1)$$

The quantities $A(\mathbf{x}, \mathbf{p})$ and $G_\epsilon(\mathbf{x}, \mathbf{p})$ are the Wigner transforms (Wigner 1932) of the projection operator $\hat{A} = |g\rangle\langle g|$ and of the molecular resolvent $\hat{G}_\epsilon = [\epsilon - \hat{H} + i0]^{-1}$ which characterizes the molecular dynamics of the nuclear degrees of freedom on a D -dimensional excited electronic potential surface. The variables \mathbf{x} and \mathbf{p} are positions and canonical momenta of the nuclear degrees of freedom. The relevant electronic dipole matrix element between initial and excited electronic state is denoted C . It is assumed to be independent of the nuclear coordinates in the relevant Franck–Condon transition region.

With the help of the semiclassical approximation the photoabsorption rate can be separated into a smooth and a rapidly frequency-dependent part (Eckhardt *et al* 1992), i.e.

$$\Gamma^{(\text{tot})}(\omega) = \Gamma^{(\text{s})}(\omega) + \Gamma^{(\text{osc})}(\omega). \quad (2)$$

The smooth part is given by

$$\Gamma^{(\text{s})}(\omega) = \frac{2\pi |\mathcal{E}C|^2}{\hbar} \int d^D x d^D p \delta(\epsilon_g + \hbar\omega - H(\mathbf{x}, \mathbf{p})) A(\mathbf{x}, \mathbf{p}). \quad (3)$$

It is the photoabsorption rate which one obtains from Fermi's golden rule by approximating the energy density of the final states on the excited electronic potential surface by the mean number of states in the relevant Franck–Condon transition volume. This volume is determined by the region in phase space in which the Wigner transform $A(\mathbf{x}, \mathbf{p})$ is localized. The mean number of states is evaluated by attributing each state a volume of magnitude $(2\pi\hbar)^D$ in phase space.

Semiclassically, the rapidly frequency-dependent part $\Gamma^{(\text{osc})}(\omega)$ is determined by properties of all classical trajectories of energy $\epsilon_g + \hbar\omega$ which leave and return again to the Franck–Condon transition region. It is given by (Eckhardt *et al* 1992)

$$\Gamma^{(\text{osc})}(\omega) = \frac{2|\mathcal{E}C|^2}{\hbar^2} \text{Re} \left\{ (2\pi i\hbar)^{-(D-1)/2} \int d^D p d^D s d^D x A(\mathbf{x}, \mathbf{p}) \right. \\ \left. \times \sum_j |\det \tilde{D}^{(j)}|^{1/2} e^{i[S_j(\mathbf{x}_f^{(j)}, \mathbf{x}_i^{(j)}) - \mathbf{p} \cdot \mathbf{s}]/\hbar - i\nu_j \pi/2} \right\}_{\mathbf{x}_f^{(j)} = \mathbf{x} + \mathbf{s}/2, \mathbf{x}_i^{(j)} = \mathbf{x} - \mathbf{s}/2}. \quad (4)$$

Thereby, the sum extends over all trajectories with initial and final positions $\mathbf{x}_i^{(j)}$ and $\mathbf{x}_f^{(j)}$ and energy $\epsilon_g + \hbar\omega$. Their classical actions are denoted $S_j(\mathbf{x}_f^{(j)}, \mathbf{x}_i^{(j)})$, ν_j counts the number of caustics on the energy shell. The matrix \tilde{D} of second derivatives is defined by

$$\tilde{D}_{kl} = \begin{pmatrix} \frac{\partial^2 S}{\partial x_i^k \partial x_j^l} & \frac{\partial^2 S}{\partial x_i^k \partial \epsilon} \\ \frac{\partial^2 S}{\partial \epsilon \partial x_j^l} & \frac{\partial^2 S}{\partial \epsilon^2} \end{pmatrix}. \quad (5)$$

For the evaluation of the integral in equation (4) we assume in the following that $\exp(i[S - \mathbf{p} \cdot \mathbf{s}]/\hbar)$ is a rapidly oscillating function of the variables \mathbf{x} and \mathbf{p} in comparison with $A(\mathbf{x}, \mathbf{p})$. Thus the dominant contributions to the integral in equation (4) come from the points of stationary phase. They correspond to trajectories with $\mathbf{s} = 0$, $\mathbf{p} = (\mathbf{p}_i + \mathbf{p}_f)/2$ and $\mathbf{p}_i = \mathbf{p}_f$, i.e. periodic orbits. The integrations in equation (4) are now accomplished by expanding the classical action up to second order around the stationary phase points but at the same time taking the \mathbf{x} - and \mathbf{p} -dependence of $A(\mathbf{x}, \mathbf{p})$ fully into account. In this way effects which originate from the finite extension of the Franck–Condon transition region

can be treated. However, then only in special cases can at least parts of the integrations which appear in equation (4) be performed analytically. One such case arises if the initially prepared vibrational state $|g\rangle$ can be modelled by a Gaussian wavefunction which may be assumed as rotationally symmetric after a suitable coordinate transformation, i.e.

$$A(\mathbf{x}, \mathbf{p}) = (\pi\hbar)^{-D} e^{-[\sigma^{-2}(\mathbf{x}-\langle\mathbf{x}\rangle)^2 + (\sigma^2/\hbar^2)\mathbf{p}^2]} \quad (6)$$

Thereby the quantity σ characterizes the extension of the Franck–Condon transition region. This approximation is applicable frequently in descriptions of molecular photoabsorption processes. Under these circumstances all integrations in equation (4), except the one along the periodic orbit, can be performed by Gaussian quadratures thus yielding

$$\Gamma^{(\text{osc})}(\omega) = \frac{2}{\hbar^2} |\mathcal{E}C|^2 (2\pi\hbar)^D \text{Re} \left\{ \sum_j e^{iS_j/\hbar - i\mu_j\pi/2} \times \int_0^{T_j} dt |\det(\mathcal{M}_j - 1)|^{-1/2} \det(\mathcal{U})_j^{-1/2} \det(\mathcal{V})_j^{-1/2} \times A(\mathbf{x}_{\text{cl}}^{(j)}, \mathbf{p}_{\text{cl}}^{(j)}) \exp \left(-\frac{\sigma^2}{\hbar^2} \mathbf{p}_{\text{cl}}^{(j)T} (\mathcal{V}_j^{-1} - 1) \mathbf{p}_{\text{cl}}^{(j)} + \frac{1}{4} \mathbf{u}_j^T (\mathcal{W}_{\perp})_j^{-1} \mathbf{u}_j \right) \right\} \quad (7)$$

The sum in equation (7) includes all periodic orbits j with classical actions S_j , orbit times T_j , Maslov indices μ_j (Eckhardt and Wintgen 1991) and coordinates and canonical momenta $(\mathbf{x}_{\text{cl}}^{(j)}(t), \mathbf{p}_{\text{cl}}^{(j)}(t))$. The vector \mathbf{u} is defined by

$$\mathbf{u} = 2\sigma^{-2} \mathbf{x}_{\perp} - (\sigma/\hbar)^2 (\mathcal{C}^T \mathcal{V}^{-1} \mathbf{p}_{\text{cl}})_{\perp}.$$

Thereby relative positions along a classical trajectory with respect to the centre of the Franck–Condon transition region, i.e. $\mathbf{x}_{\text{cl}}(t) - \langle\mathbf{x}\rangle$, have been split up into a part oriented along the periodic orbit and an orthogonal projection $\mathbf{x}_{\perp}(t)$. The corresponding orthogonal part of a matrix \mathcal{N} is denoted \mathcal{N}_{\perp} . The matrices \mathcal{U} , \mathcal{V} and \mathcal{W} are defined by

$$\begin{aligned} \mathcal{U} &= 1_{\perp} + 2i\hbar(\mathcal{B}_{\perp})^{-1} \sigma^{-2} + i\sigma^2(\mathcal{B}_{\perp})^{-1} (\mathcal{C}^T \mathcal{V}^{-1} \mathcal{C})_{\perp} / (2\hbar) \\ \mathcal{V} &= 1 - i\sigma^2 \mathcal{A} / (2\hbar) \\ \mathcal{W} &= \sigma^{-2} 1 - i\mathcal{B} / (2\hbar) + (\sigma/2\hbar)^2 \mathcal{C}^T \mathcal{V}^{-1} \mathcal{C} \end{aligned} \quad (8)$$

whereby the matrices \mathcal{A} , \mathcal{B} and \mathcal{C} are given by

$$\begin{aligned} \mathcal{A}_{kl} &= \frac{\partial^2 S}{\partial x_f^k \partial x_f^l} + \frac{\partial^2 S}{\partial x_i^k \partial x_i^l} - \frac{\partial^2 S}{\partial x_f^k \partial x_i^l} - \frac{\partial^2 S}{\partial x_i^k \partial x_f^l} \\ \mathcal{B}_{kl} &= \frac{\partial^2 S}{\partial x_f^k \partial x_f^l} + \frac{\partial^2 S}{\partial x_i^k \partial x_i^l} + \frac{\partial^2 S}{\partial x_f^k \partial x_i^l} + \frac{\partial^2 S}{\partial x_i^k \partial x_f^l} \\ \mathcal{C}_{kl} &= \frac{\partial^2 S}{\partial x_f^k \partial x_f^l} - \frac{\partial^2 S}{\partial x_i^k \partial x_i^l} + \frac{\partial^2 S}{\partial x_f^k \partial x_i^l} - \frac{\partial^2 S}{\partial x_i^k \partial x_f^l} \end{aligned} \quad (9)$$

The calculation of the derivatives and their relation to monodromy matrix elements is outlined in Gutzwiller (1971) and Zobay (1992). The matrix \mathcal{M} in equation (7) denotes the orthogonal part of the monodromy matrix of the periodic orbits. All these quantities

have to be evaluated along the periodic orbits j which cross the Franck–Condon transition region and thus contribute to equation (7) significantly.

The semiclassical expression for $\Gamma^{(\text{osc})}(\omega)$ of equation (7) is a main result of this letter. For a Gaussian initial state $A(\mathbf{x}, \mathbf{p})$ it generalizes previously obtained results of Eckhardt *et al* (1992) as it takes into account effects originating from a finite extension of the Franck–Condon transition region in phase space in comparison with the extensions of the Fresnel zones of the relevant periodic orbits. These effects are described by the matrices \mathcal{U} , \mathcal{V} and \mathcal{W} which depend essentially on the transverse monodromy matrix elements which characterize the extension of the Fresnel zone of a contributing periodic orbit (Kravtsov and Orlov 1990). The limit of a large Franck–Condon transition region, which corresponds to the results of Eckhardt *et al* (1992), is obtained by letting $u \rightarrow 0$, $\mathcal{U} \rightarrow 1$, $\mathcal{V} \rightarrow 1$ and $\mathcal{W} \rightarrow -i\mathcal{B}/(2\hbar)$. However, in molecular photoabsorption processes with an initial Gaussian state this limit is difficult to realize. This is due to the fact that in general at best the \mathbf{x} - or the \mathbf{p} -dependence of $A(\mathbf{x}, \mathbf{p})$ is sufficiently smooth but not both of them at the same time. In the following this aspect is demonstrated by describing photoabsorption of the CO_2 molecule with the help of the semiclassical formulae of equations (3) and (7).

The collinear model of the CO_2 molecule as introduced by Kulander and Light (1980) has played an important role in the understanding of ‘diffuse’ photoabsorption spectra (Herzberg 1966) of symmetric collinear triatomic molecules (Pack 1976, Kulander and Light 1980, Schinke and Engel 1990, Kulander *et al* 1991). Within this model the Hamiltonian which describes the dynamics of the nuclear degrees of freedom on the excited electronic potential surface $V(x_1, x_2)$ is given by (Kulander and Light 1980)

$$\hat{H} = \frac{1}{2\mu}(\hat{p}_1^2 + \hat{p}_2^2) - \frac{1}{m_{\text{O}}} \hat{p}_1 \hat{p}_2 + V(\hat{x}_1, \hat{x}_2) \quad (10)$$

with the reduced mass $\mu = m_{\text{O}}m_{\text{C}}/(m_{\text{O}} + m_{\text{C}})$ and the masses of O and C denoted m_{O} and m_{C} . The distances between O–C and C–O in the collinear configuration are x_1 and x_2 . The two-dimensional potential surface $V(x_1, x_2)$ is approximated by a repulsive LEPS potential (Sato 1955). In the following the initially prepared vibrational state $|g\rangle$, from which the photoabsorption process starts, is modelled by spherically symmetric Gaussian wavefunctions with $D = 2$, $\langle x_1 \rangle = \langle x_2 \rangle = 2.095$ au or $\langle x_1 \rangle = \langle x_2 \rangle = 2.205$ au and $\sigma = 0.085$ au (Schinke and Engel 1990) (compare with equation (6)).

Numerical time-dependent calculations of the photoabsorption process (Schinke and Engel 1990, Kulander *et al* 1991) show that the main contributions to the oscillating structure in the spectrum originate from trajectories with recurrence times below 95 fs. We have found four important classes of periodic orbits which cross the Franck–Condon transition region with suitable orbit times and energies. In figure 1 these classes are denoted I–IV and are shown together with equipotential lines of the electronic potential surface. The relation between classical periodic orbits of the type I–III and the photoabsorption rate has already been established on a qualitative level by comparison of their orbit times with the corresponding recurrence times of the time-dependent autocorrelation function (Schinke and Engel 1990, Kulander *et al* 1991). The periodic orbits of class IV have not been considered explicitly in this context, so far. However, on the basis of equation (7) the photoabsorption rate can now be evaluated directly from a knowledge of classical properties of these periodic orbits thus exhibiting the *quantitative* connection between classical dynamics on a potential surface and the photoabsorption rate.

In figure 2(a)–(d) the semiclassical photoabsorption rate of CO_2 as evaluated from equations (3) and (7) with the help of the classes of periodic orbits of figure 1 is compared

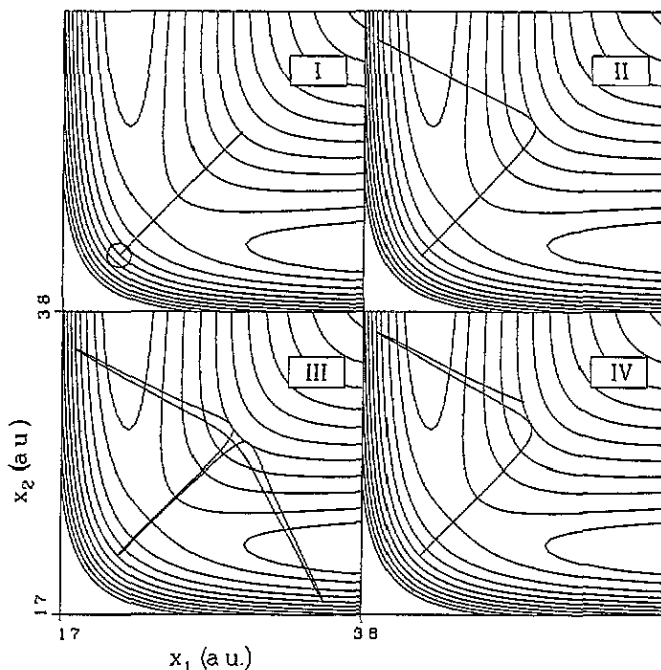


Figure 1. Contour plots of the excited electronic potential surface of the collinear model of CO_2 with periodic orbits of classes I–IV (a–d). As to the classes II and IV also the orbits which arise by a reflection of the trajectories shown at the diagonal $x_1 = x_2$ have to be considered in the calculation. The circle in the first plot is centred around $\langle x_1 \rangle = \langle x_2 \rangle = 2.095$ au with radius $\sigma = 0.085$ au and indicates the extension of the initial state $|g\rangle$.

with the corresponding result of a numerical quantum mechanical calculation as performed previously by Schinke and Engel (1990). In figure 2(a) and (b) the oscillating part of the photoabsorption rate is shown for the two initial Gaussian states centred around $\langle x_1 \rangle = \langle x_2 \rangle = 2.205$ au (a) and $\langle x_1 \rangle = \langle x_2 \rangle = 2.095$ au (b) with $\sigma = 0.085$ au. The semiclassical results of equation (7) (broken curves) are close to the numerical results (full curves). The corresponding results of the semiclassical periodic-orbit formula of Eckhardt *et al* (1992) are inserted on the upper right of these figures (broken curves). The comparison of the two semiclassical approximations indicates the importance of effects originating from the finite extension of the Franck–Condon transition region in comparison with the extensions of the Fresnel zones of the contributing periodic orbits. Semiclassical (broken curves) and numerical (full curves) total photoabsorption rates $\Gamma^{(\text{tot})}(\omega)$ and smooth contributions $\Gamma^{(\text{s})}(\omega)$ are shown in figure 2(c) and (d) for $\langle x_1 \rangle = \langle x_2 \rangle = 2.095$ au and $\sigma = 0.085$ au.

The orbit classes III and IV have comparable orbit times. Therefore quantum mechanical interferences between their probability amplitudes manifest themselves in the photoabsorption process. This is apparent from figure 2(e) where the time dependence of the autocorrelation function $|\langle g|\psi(t)\rangle|$ is shown. With the help of equation (7) the contribution of each of these two classes of periodic orbits can be evaluated in a straightforward way (chain curves). This example shows that the used semiclassical methods are well suited for establishing a quantitative one-to-one correspondence between contributions of periodic orbits and structures in molecular photoabsorption rates or autocorrelation functions.

In conclusion, by concentrating on a collinear model of the CO_2 molecule we have shown that photoabsorption rates can be understood semiclassically on a quantitative level

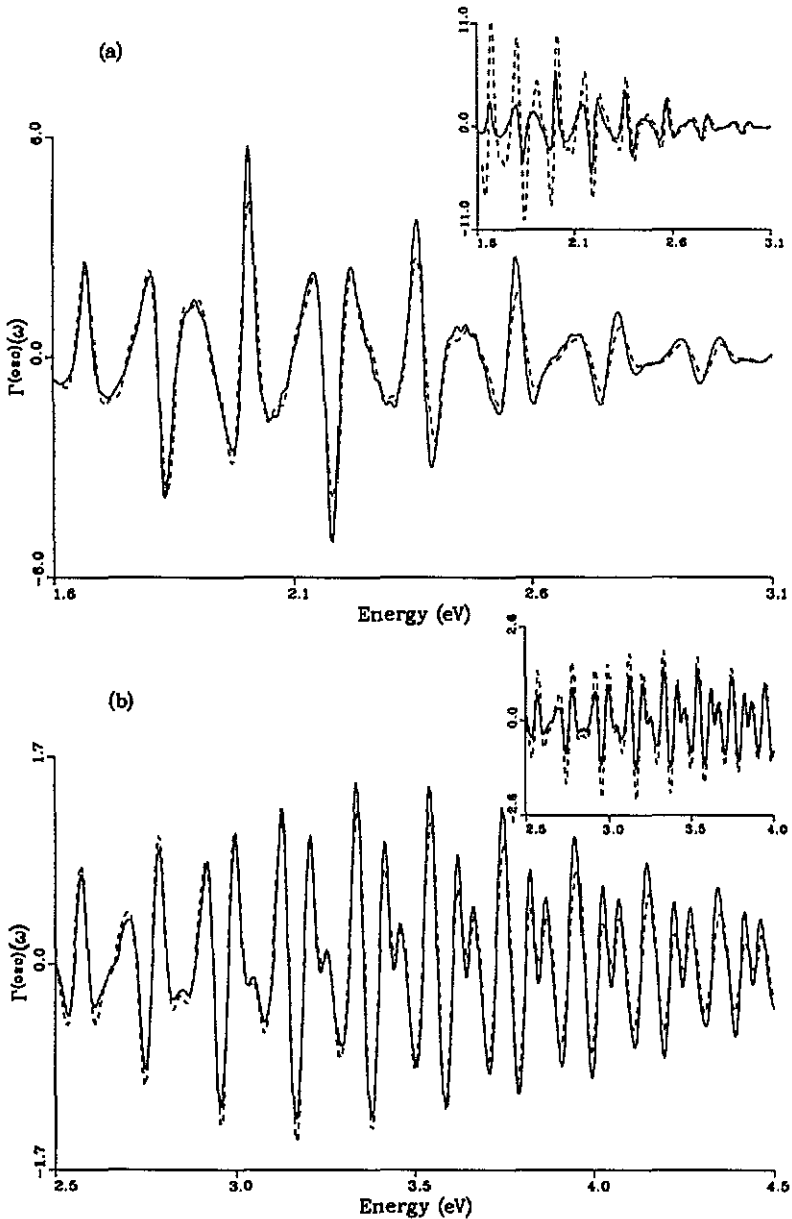


Figure 2. Photoabsorption rate $\Gamma(\omega)$ of the collinear CO_2 molecule in units of $2\pi|\mathcal{E}C|^2/\hbar$: exact quantum mechanical results (full curves), semiclassical calculations according to equations (3) and (7) (broken curves), semiclassical results of Eckhardt *et al* (1992) are inserted on the upper right (broken curves). (a), (b), oscillating contribution $\Gamma^{(\text{osc})}(\omega)$ of periodic orbits of classes I, II and III + IV; (c), (d), total rate $\Gamma^{(\text{tot})}(\omega)$ and smooth contribution $\Gamma^{(\text{s})}(\omega)$. (e), autocorrelation function for times between 75 and 95 fs. (a) is valid for the initial Gaussian state with $\langle x_1 \rangle = \langle x_2 \rangle = 2.205$ au, (b)–(e) for the initial state centred at 2.095 au.

in terms of contributions of classical periodic orbits. The resulting semiclassical one-to-one correspondence between periodic orbits and photoabsorption rates gives interesting insights into the connection between the classical and the corresponding quantum dynamics

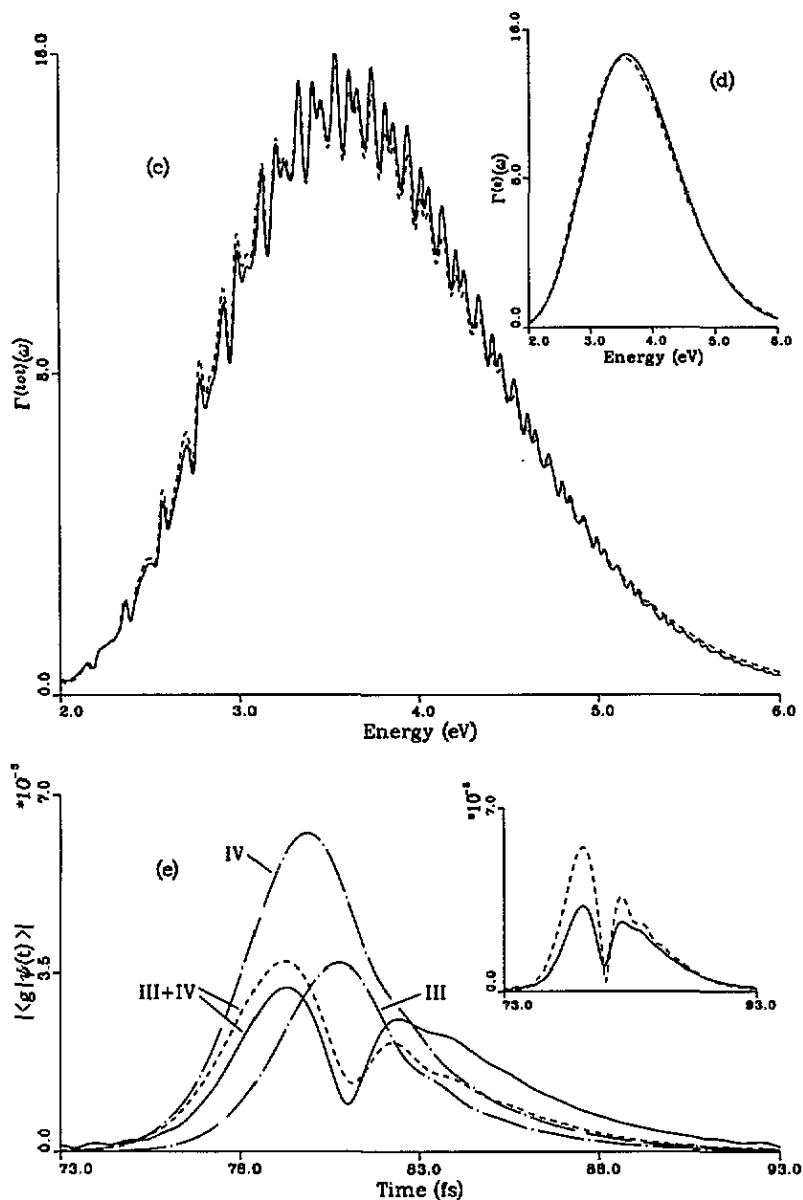


Figure 2. (Continued)

of nuclear degrees of freedom on an excited electronic potential surface. A generalization of results previously obtained by Eckhardt *et al* (1992) has been presented which shows that for a satisfactory semiclassical description effects originating from a finite extension of the Franck–Condon transition region in comparison with the extension of the relevant Fresnel zones of contributing periodic orbits have to be taken into account.

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