



**Figure 6.** A plot of the  $S_1$  vibrational level density against vibrational energy for pDFB. The indicated density considers only the gerade levels and is half of the total level density. Since there are eight vibrational symmetry classes in pDFB, the density of any single symmetry class will be approximately one-eighth of the total density. The positions and identities of the levels examined in the present study are shown on the plot.

ditional oxygen. A kinetic analysis including both the collisional relaxation and the collision-free IVR reproduces quantitatively the relative intensities of structured and background emission.<sup>17</sup>

#### Concluding Remarks

This search for IVR dynamics is summarized in Figure 6, which shows a plot of the density of  $S_1$  vibrational levels against vibrational energy. It can be seen that the 11 studied levels represent a fairly even energy spacing in the encompassed range. Indications of a dynamic IVR are observed for every level. IVR appears to

(17) Holtzclaw, K. W. Ph.D. Thesis, Indiana University, Bloomington, IN, 1984.

be a general property of  $S_1$  levels in pDFB, at least above  $\epsilon_{\text{vib}} \approx 1600 \text{ cm}^{-1}$ . No levels have been found above this energy for which indications of IVR are absent.

There is no obvious reason why pDFB would in any way be exceptional among polyatomics. In fact, a similar but less encompassing probe of IVR in *p*-fluorotoluene reveals an analogous behavior.<sup>11,18</sup> These results combined with the ubiquitous onsets of congested emission in the collision-free spectra<sup>3</sup> of many polyatomics is suggestive. The dynamic process of IVR may well be the rule among levels low in the  $S_1$  vibrational manifold of aromatics.

The plot in Figure 6 also emphasizes the extraordinarily low level densities at which IVR can operate. The accessible vibrational level densities may be even lower. The densities reported in Figure 6 are one half the total level density. That value corresponds to the assumption that the only symmetry restriction on coupling is the gerade-ungerade prohibition. If, as is probable, the symmetry restrictions are more severe, the accessible density will be further reduced. For example, if only a single symmetry species can couple to the initially prepared level, the accessible density will be about one-fourth of that shown in the figure.<sup>19</sup>

The lower levels in our study involve a state density near one level per  $\text{cm}^{-1}$ . Dynamic IVR can occur only if levels overlap by their homogeneous widths or if a set of levels is coherently pumped. The sparse vibrational density would appear to preclude IVR in our experiments as well as those of Moore et al.<sup>5,6</sup> and of Halberstadt and Tramer.<sup>7</sup> It seems imperative that an additional source of level density is available to these room temperature systems. The most probable candidates are rovibronic levels made accessible by Coriolis rotation-vibration coupling.

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(18) Stone, B. M., Ph.D. Thesis, Indiana University, Bloomington, IN, 1984.

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## Self-Consistent Gaussian Wavepackets in Semiclassical Molecular Dynamics

Shaul Mukamel†

Department of Chemistry, University of Rochester, Rochester, New York 14627 (Received: April 25, 1984)

An algorithm for the propagation of wavepackets in nonlinear (anharmonic) potentials is developed. The information contained in a chosen set of dynamical variables is retained, and self-consistent, formally exact, reduced equations of motion (REM) are derived for these quantities. As a special case, we analyze the use of Gaussian wavepackets by focusing on the first two moments of coordinates and momenta, *i.e.*,  $\langle x \rangle$ ,  $\langle p \rangle$ ,  $\langle x^2 \rangle$ , and  $\langle p^2 \rangle$ . For anharmonic systems, the REM contain "mean field" terms which assume that the wavepacket is Gaussian at all times and fluctuation terms arising from deviations of the actual wavepacket from Gaussian. It is essential to retain the latter terms in order to allow the Gaussian wavepacket to have the correct first and second moments.

### I. Introduction

The evaluation of the propagator  $\exp(-iHt)$  is a key step in any calculation of molecular dynamics and spectroscopy. It is well-known that, when the potentials of interaction contain only terms linear and quadratic in the coordinates (e.g., harmonic systems),

the propagator, in the coordinate representation, assumes a simple Gaussian form. Consequently, if the wave function is Gaussian at  $t = 0$ , it will remain so for all later times.<sup>1</sup> It was proposed by Heller<sup>2</sup> to use Gaussian wavepackets even for more realistic

† Alfred P. Sloan fellow, Camille and Henry Dreyfus Teacher-Scholar.

(1) R. P. Feynman and A. R. Hibbs, "Quantum Mechanics and Path Integrals", McGraw-Hill, New York, 1965.

potentials, by making a local expansion of the potential surface and retaining quadratic terms. This results in a simple set of equations for the parameters characterizing the Gaussian.

In this Letter, we consider this algorithm from the perspective of nonequilibrium statistical mechanics. Given the actual wave function of the system, we introduce a Gaussian wavepacket which has the correct first and second moments of the coordinates and momenta  $\langle x \rangle$ ,  $\langle p \rangle$ ,  $\langle x^2 \rangle$ , and  $\langle p^2 \rangle$ . Exact reduced equations of motion (REM) for the time evolution of this wavepacket are then derived. The REM are self-consistent and guarantee that the first two moments are exact. They contain two terms: The first is a "mean field" type and arises if we assume that the wave function remains Gaussian at all times. The second is a fluctuation type term arising from the deviations of the actual wave function from a Gaussian form. In section II we develop the basic REM which allow us to propagate an arbitrary wavepacket by keeping any desired number of dynamical variables. In section III we focus on the first two moments, specify the REM for Gaussian wavepackets, and analyze the resulting equations.

## II. The Reduced Equations of Motion

We shall now derive the reduced equations of motion which form the basis for our expansion. We consider a system characterized by a Hamiltonian  $H$  and a density matrix  $\rho$  which obeys the Liouville equation

$$d\rho/dt = -i[H, \rho] \equiv -iL\rho \quad (1)$$

$L$  being the Liouville operator. We shall adopt a Liouville space notation in which an ordinary operator is represented by a ket  $|H\rangle$ ,  $|\rho\rangle$ , etc. We further define a scalar product of two operators as

$$\langle\langle A|B\rangle\rangle \equiv \text{Tr}(A^\dagger B) \quad (2)$$

(For brevity, we set  $\hbar = 1$  in this section.) Usually the complete density matrix  $\rho(t)$  is very complicated and it will be impractical to attempt to calculate it in full detail. Let us focus instead on a small set of dynamical variables of interest  $A_i$ ,  $i = 0, 1, \dots, N$  where  $A_0 \equiv 1$  is the unit operator and the remaining  $N$  operators are chosen depending on the level of detail in which we wish to construct our reduced description. We shall denote the expectation values of these operators by  $\sigma_i(t)$ , i.e.

$$\sigma_i(t) \equiv \langle\langle \rho(t)|A_i\rangle\rangle \equiv \text{Tr}(\rho(t)A_i) \quad i = 0, 1, \dots, N \quad (3)$$

Note that the normalization implies  $\sigma_0 = 1$ . Let us further construct a simplified density matrix  $\sigma(t)$  (which we may choose in a variety of ways) such that it satisfies the constraints of eq 3, i.e.

$$\sigma_i(t) = \langle\langle \sigma(t)|A_i\rangle\rangle \equiv \text{Tr}(\sigma(t)A_i) \quad (4)$$

Normally,  $\sigma(t)$  will depend on  $N + 1$  parameters which are chosen to satisfy the  $N + 1$  conditions (4). The conventional choice in nonequilibrium statistical mechanics is the maximum entropy, i.e.<sup>3-7</sup>

$$\sigma(t) = \exp\left[\sum_{i=0}^N \lambda_i(t)A_i\right] \quad (5)$$

$\lambda_i$  being determined by eq 4. However, formally we may choose any distribution  $\sigma(t)$  which satisfies eq 4. Let us further define the following  $(N + 1) \times (N + 1)$  matrix

$$S(t)_{ij} \equiv \langle\langle A_i|\sigma(t)A_j\rangle\rangle \equiv \text{Tr}(A_i^\dagger \sigma(t)A_j) \quad (6)$$

and the operator<sup>5</sup>

$$P(t) \equiv \sum_{i,j=0}^N |\sigma(t)A_i\rangle\langle A_j| S^{-1}(t)_{ij} \quad (7)$$

It is easy to show that  $P(t)$  is a projection operator in Liouville space and has several interesting properties

$$(i) \quad P(t)P(t') = P(t) \quad (8a)$$

A special case of (i) is  $P^2(t) = P(t)$ , which is a necessary condition for  $P$  to be a projection operator.

$$(ii) \quad P(t)\rho(t) = \sigma(t) \quad (8b)$$

$$(iii) \quad \langle\langle A_m|P(t)\dot{\rho}(t)\rangle\rangle = \langle\langle A_m|\dot{\sigma}(t)\rangle\rangle \quad (8c)$$

$\dot{\rho}$  being  $d\rho/dt$  and  $\dot{\sigma}$  is  $d\sigma/dt$ .

$$(iv) \quad P(t)|\sigma(t)A_n\rangle = |\sigma(t)A_n\rangle \quad (8d)$$

properties (i) and (iv) follow directly from the definitions (6) and (7). (ii) and (iii) are proven in Appendix A.  $P(t)$  therefore projects the complicated density matrix  $\rho(t)$  onto the simpler distribution  $\sigma(t)$ . Suppose now that at some initial time  $t = t'$  we have

$$\rho(t') \equiv \sigma(t'). \quad (9)$$

In general,  $\rho(t)$  for  $t > t'$  will not be equal to  $\sigma(t)$ . Using assumption (9) we derive, in Appendix B, the following exact REM for  $\sigma_i(t)$ .<sup>4,7</sup>

$$\dot{\sigma}_m(t) = -i\langle\langle A_m|L|\sigma(t)\rangle\rangle + \sum_{l=0}^N K_{ml}(t,t')\sigma_l(t) \quad (10)$$

Here

$$\mathbf{K}(t,t') \equiv \mathbf{W}(t,t')\mathbf{V}^{-1}(t,t') \quad (10a)$$

$$W_{mn}(t,t') = -i\langle\langle A_m|LQ(t)U(t,t')|\sigma(t')A_n\rangle\rangle \quad (10b)$$

$$V_{ki}(t,t') = \langle\langle A_k|U(t,t')|\sigma(t')A_i\rangle\rangle \quad (10c)$$

$$Q(t) \equiv 1 - P(t) \quad (10d)$$

is the complementary projection to  $P(t)$ . Also

$$U(t,t') = \exp[-iL(t-t')] \quad (10e)$$

Equations 10 are exact. These are  $N$  equations for the  $N$  unknowns  $\sigma_i(t)$   $i = 1, \dots, N$  (note that  $\sigma_0 = 1$ ). These equations are nonlinear since  $\sigma(t)$  and  $\mathbf{K}(t,t')$  depend on  $\sigma_i(t)$  in a nonlinear way. The first term in eq 10 is a "mean field" term which arises if  $\rho(t) = \sigma(t)$  for all times. In that case  $Q(t)\rho(t) = 0$  and consequently  $\mathbf{K}(t,t') = 0$ . The second term arises from the fact that  $\rho(t) \neq \sigma(t)$  for  $t > t'$ , and corrects the time evolution of  $\sigma(t)$ . We further note that eq 10 is time local unlike the more conventional equations which are memory type.<sup>4-6</sup> These type of equations were explored extensively in several fields.<sup>8,9</sup> The key step in utilizing eq 10 is to develop some approximate scheme for evaluating the kernel  $\mathbf{K}$ . This will be discussed briefly below.

## III. Application to Gaussian Wavepackets

We are now in a position to apply eq 10 to develop an approximation for the quantum mechanical propagator. For simplicity in the notation we specialize to a single degree of freedom  $x$ . The generalization to multidimensional systems is straightforward. Let us consider the following four relevant variables:

$$A_1 = x \quad (11a)$$

$$A_2 = p \quad (11b)$$

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(9) S. Mukamel, *Phys. Rev. B*, **25**, 830 (1982); *J. Stat. Phys.*, **27**, 317 (1982); **30**, 179 (1983); S. Mukamel and D. Grimbirt, *Opt. Commun.*, **40**, 421 (1982).

(2) E. J. Heller, *J. Chem. Phys.*, **62**, 1544 (1975); *Acc. Chem. Res.*, **14**, 368 (1981).

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(4) E. T. Jaynes, *Phys. Rev.*, **106**, 620 (1957); **108**, 171 (1957).

(5) B. Robertson, *Phys. Rev.*, **144**, 151 (1966); **160**, 175 (1967).

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(7) R. D. Levine and M. Tribus, Eds., "The Maximum Entropy Formalism", MIT Press, Cambridge, 1979.

$$A_3 = x^2 \quad (11c)$$

$$A_4 = p^2 \quad (11d)$$

We shall be interested in following the time evolution of these variables. To that end we construct the following Gaussian wavepacket  $\psi_0(x)$ :

$$\langle x|\psi_0(t)\rangle = \left(\frac{2\alpha_1}{\pi\hbar}\right)^{1/4} \exp\left[\frac{i}{\hbar}\alpha(x-\bar{x})^2 + \frac{i}{\hbar}\bar{p}(x-\bar{x}) + \frac{i}{\hbar}\gamma\right] \quad (12)$$

Here  $\bar{x}$ ,  $\bar{p}$ , and  $\gamma$  are real whereas  $\alpha$  is complex, i.e.

$$\alpha = i\alpha_1 + \alpha_2 \quad (12a)$$

All these parameters are time dependent. The density operator  $\sigma(x, x')$  corresponding to  $\psi_0$  is

$$\sigma(x, x', t) \equiv \langle x|\psi_0(t)\rangle\langle\psi_0(t)|x'\rangle \quad (13)$$

i.e.

$$\sigma(x, x', t) = \left(\frac{2\alpha_1}{\pi\hbar}\right)^{1/2} \exp\left\{-\frac{\alpha_1}{\hbar}[(x-\bar{x})^2 + (x'-\bar{x})^2] + \frac{i}{\hbar}\alpha_2[(x-\bar{x})^2 - (x'-\bar{x})^2] + \frac{i}{\hbar}\bar{p}(x-\bar{x})\right\} \quad (14)$$

Note that the phase  $\gamma$  does not appear in  $\sigma$ . The four real parameters  $\bar{x}$ ,  $\bar{p}$ ,  $\alpha_1$ , and  $\alpha_2$  may be determined via eq 4 where  $A_i$  are the operators defined in eq 11, i.e.

$$\sigma_1(t) \equiv \langle x(t)\rangle = \bar{x}(t) \quad (15a)$$

$$\sigma_2(t) \equiv \langle p(t)\rangle = \bar{p}(t) \quad (15b)$$

$$\sigma_3(t) - \sigma_1^2(t) = \langle x^2(t)\rangle - \langle x(t)\rangle^2 = \frac{\hbar}{4\alpha_1(t)} \quad (15c)$$

$$\sigma_4(t) - \sigma_2^2(t) = \langle p^2(t)\rangle - \langle p(t)\rangle^2 = \frac{\hbar|\alpha(t)|^2}{\alpha_1(t)} \quad (15d)$$

When eq 14 together with eq 15 is substituted in eq 10 we obtain the desired self-consistent equation for the propagation of the Gaussian wavepacket with the *exact* values of the first two moments. Note that by eq 15 the parameters  $\sigma_1$ ,  $\sigma_2$ ,  $\sigma_3$ , and  $\sigma_4$  carry the same information as  $\bar{x}$ ,  $\bar{p}$ ,  $\alpha_1$ , and  $\alpha_2$  and we may express the equations in terms of either set of variables.

We are now in a position to discuss the significance of our results:

(a) The procedure suggested by Heller<sup>2</sup> is obtained from our equations if we make the following approximations:

(i) Neglect the fluctuation term  $K$  completely (i.e., assume that the true density matrix  $\rho(t)$  is Gaussian at all times). Equations 10 then assume the form

$$\dot{\sigma}_m(t) = -\frac{i}{\hbar} \text{Tr} [A_m H \sigma(t) - A_m \sigma(t) H] \quad m = 1, \dots, 4 \quad (16)$$

where  $\sigma(t)$  is given by eq 14 and  $A_m$  were defined in eq 11.

(ii) Make a harmonic expansion for  $H$ , i.e., expand it in coordinates retaining only quadratic terms. This result is<sup>2</sup>

$$\frac{d\bar{x}}{dt} = \frac{\partial H}{\partial \bar{p}} \quad (17a)$$

$$\frac{d\bar{p}}{dt} = -\frac{\partial H}{\partial \bar{x}} \quad (17b)$$

$$\frac{d\alpha}{dt} = -\frac{2}{m}\alpha^2 - \frac{1}{2}\frac{d^2V}{dx^2} \quad (17c)$$

Here,  $V(x)$  is the interaction potential and the derivatives in eq 17 are taken at  $x = \bar{x}$ ,  $p = \bar{p}$ . As is clear from our present analysis, eq 17 are valid for harmonic systems. Once anharmonicities are introduced, these equations do not have the correct self-consistent values for  $\bar{x}$ ,  $\bar{p}$ ,  $\langle x^2 \rangle$ , and  $\langle p^2 \rangle$  due to approximations (i) and (ii) made above. Approximation (i) may be quite severe since the

error associated with it may grow rapidly with time. A further analysis is required in order to justify the usage of eq 17 for realistic anharmonic systems.

(b) In eq 17,  $\bar{x}$  and  $\bar{p}$  obey simply the classical equations of motion and are not affected by the second moments  $\langle x^2 \rangle$  and  $\langle p^2 \rangle$ . The self-consistent eq 10 will in general couple all four moments and will allow the second moments to affect the first moments.

(c) Equations 17 may be generalized in two ways. We can either add higher moments  $\langle x^3 \rangle$ ,  $\langle p^3 \rangle$ , etc. by taking a more elaborate wavepacket with more parameters. This will increase the number of equations. Alternatively, we may retain the Gaussian form but then we have to expand eq 10 perturbatively in anharmonicities or in  $\hbar$  in order to get a self-consistent Gaussian wavepacket.

(d) An alternative self-consistent method based on a nonlinear Fokker-Planck equation was developed recently toward obtaining a Gaussian approximation which has the correct second-order correlation function (and the spectrum).<sup>10</sup> That procedure is based on constructing an effective harmonic system with more degrees of freedom which has the same correlation function as the original anharmonic system.

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## Appendix A

Equation 8b may be derived by starting from eq 7, i.e.

$$P(t)|\rho(t)\rangle\rangle = \sum_{ij} |\sigma(t) A_i\rangle\rangle S^{-1}(t)_{ij} \langle\langle A_j|\rho(t)\rangle\rangle \quad (A1)$$

Note, however, that from eq 3 and 4 we have

$$\langle\langle A_j|\rho(t)\rangle\rangle = \langle\langle A_j|\sigma(t)\rangle\rangle = \langle\langle A_j|\sigma(t)A_0\rangle\rangle \equiv S_{j0}(t) \quad (A2)$$

Also

$$\sum_j S^{-1}(t)_{ij} S_{j0}(t) = \delta_{i,0} \quad (A3)$$

Upon the substitution of eq A2 and A3 in eq A1 we get eq 8b. Equation 8c may be obtained by starting from

$$\langle\langle A_m|P(t)|\rho(t)\rangle\rangle = \sum_{k,l} \langle\langle A_m|\sigma(t)A_k\rangle\rangle S_{kl}^{-1}(t) \langle\langle A_l|\rho(t)\rangle\rangle \quad (A4)$$

Note that from eq 3 and 4 we have

$$\langle\langle A_l|\rho(t)\rangle\rangle = \frac{d}{dt} \langle\langle A_l|\sigma(t)\rangle\rangle = \langle\langle A_l|\dot{\sigma}(t)\rangle\rangle \quad (A5)$$

Also from eq 6

$$\langle\langle A_m|\sigma(t)A_k\rangle\rangle = S(t)_{mk} \quad (A6)$$

Substitution of eq A5 and A6 in eq A4 results in eq 8c.

## Appendix B

Imagine a time  $t'$  whereby

$$\rho(t') = P(t') \rho(t') = \sigma(t') \quad (B1)$$

Let us write the formal solution of the Liouville eq 1

$$\rho(t) = U(t, t') \rho(t') \quad (B2)$$

where

$$U(t, t') = \exp[-iL(t - t')] \quad (B3)$$

Multiplying both sides of eq B2 by  $P(t)$  and recalling eq B1 we get

$$\sigma(t) = P(t) \rho(t) = P(t) U(t, t') P(t') \rho(t') \quad (B4)$$

Multiplying by  $A_m^\dagger$  from the left and taking a trace we get

$$\sigma_m(t) = \sum_{n,l} \langle\langle A_m|U(t, t')|\sigma(t')A_n\rangle\rangle S^{-1}(t)_{nl} \sigma_l(t') \quad (B5)$$

We shall now consider  $\dot{\rho}(t)$ :

$$\dot{\rho}(t) = -iLU(t,t')\rho(t') \quad (\text{B6})$$

Again multiplying both sides by  $P(t)$  and using eq B1 we get

$$P(t)\dot{\rho}(t) = -iP(t)L U(t,t')P(t')\rho(t') \quad (\text{B7})$$

Multiplying both sides by  $A_m^\dagger$  from the left and taking a trace, we get

$$\dot{\sigma}_m(t) = i\langle\langle A_m|L U(t,t')|\sigma(t')A_n\rangle\rangle S^{-1}(t')_{nl}\sigma_l(t') \quad (\text{B8})$$

where we have used eq 7.

Equations B5 and B8 form the basis for our REM. We now solve eq B5 for  $\sigma(t')$  and substitute it in eq B8 resulting in

$$\dot{\sigma}_m(t) = -i\sum_{n,l}\langle\langle A_m|LU(t,t')|\sigma(t')A_n\rangle\rangle\langle\langle A|U(t,t')|\sigma(t')A\rangle\rangle^{-1}_{nl}\sigma_l(t') \quad (\text{B9})$$

Inserting  $P(t) + Q(t)$  between  $L$  and  $U$  in eq B9 (note that  $P + Q = 1$ ), results in eq 10.

## FEATURE ARTICLE

### Photoelectron Dynamics of Molecules<sup>†</sup>

V. McKoy,\*

Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology,  
Pasadena, California 91125

T. A. Carlson,

Oak Ridge National Laboratory, Chemistry Division, Oak Ridge, Tennessee 37830

and R. R. Lucchese

Department of Chemistry, Texas A & M University, College Station, Texas 77843  
(Received February 17, 1984)

Unlike earlier studies of photoelectron spectroscopy which were carried out with traditional light sources, the availability of intense tunable radiation provided by synchrotron sources has made possible remarkable progress in the characterization of the important dynamical aspects of molecular photoionization. In this article we review both the current experimental thrust in molecular photoionization and the theoretical models which are being developed to adequately describe the important new features which emerge from these experiments. Progress in this area continues to reveal the rich dynamical content of molecular photoionization.

#### Introduction

Molecular photoelectron spectroscopy came into prominence with the studies of Turner and his co-workers<sup>1</sup> in the early 1960s. The main purpose of these studies of photoelectron spectroscopy was to characterize a molecule in terms of a simple energy level scheme based on molecular orbitals. Although these earlier studies contributed significantly to our understanding of both molecular electronic structure and of photoelectron dynamics,<sup>2</sup> they were carried out with traditional light sources and hence did not provide photoelectron spectra over a continuous range of photon energy. Measurements of these photoelectron spectra over a continuous and wide range of photon energies are clearly needed to characterize the dynamical aspects of the molecular photoionization process. Synchrotron radiation provides the intense tunable source of photons needed to study the continuous variation of atomic and molecular photoionization cross sections with photon energy. The increasing availability of synchrotron radiation, coupled with the advent of high-resolution, angle-resolving electron spectrometers, is making it possible to study the structure and dynamics of the electronic continua of atoms and molecules at a highly differentiated level.<sup>3</sup> Such experiments, along with related theoretical developments, have led to remarkable progress in our under-

standing of the dynamics of molecular photoionization processes.

The main purpose of this article is to review the highlights of recent progress in the experimental and theoretical studies of molecular photoionization. This article is not intended to present a detailed account and critical assessment of developments in this field but is written in the form of an informative survey of both the current experimental thrust in molecular photoionization and the theoretical models which are being developed to adequately describe the important new features which are emerging from these experiments. We shall see that shape resonances or quasi-bound states in which an electron is temporarily trapped by a potential barrier play an important role in molecular photoionization and lead to very pronounced dynamical features in the photoelectron spectrum.<sup>4</sup> Although similar barriers are known in atomic systems, the nonspherical force fields of molecules can lead to very

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