Periodic orbit—Quantum mechanical investigation of the inversion mechanism of Ar₃

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The inversion mechanism of a T-shaped Ar₃ is studied both classically and quantum mechanically. Regular states, localized in the region of the transition state for the inversion of the axial argon atom are found and are assigned by the symmetric stretch stable periodic orbits which emanate from the saddle point of the potential. These states inhibit the inversion process. States which promote the inversion are mainly irregular, but a few of them are localized and they have their nodes perpendicularly arranged along periodic orbits which originate from saddle node bifurcations. The two types of periodic orbits, inhibiting and isomerizing, are used to produce distinctly different spectra and to extract the corresponding eigenfunctions by solving the time dependent Schrödinger equation using a variable order finite difference method [J. Chem. Phys. 111, 10827 (1999), preceding paper]. © 1999 American Institute of Physics. [S0021-9606(99)30247-6]

I. INTRODUCTION

One elementary chemical reaction is the inversion of a molecule. Generally, inversion may be seen as an isomerization reaction between two equivalent minimum energy conformations which correspond to two symmetric minima on the potential energy surface (PES). Isomerization occurs by exciting the molecule to a vibrational state which has appreciable probability amplitude in both minima. At energies where the molecule isomerizes the motions of atoms are expected to be irregular because of the nonlinearity and coupling of the potential function¹ close to and above the barrier of isomerization.

The progress of high resolution spectroscopy at excited vibrational states in the last years reveals that, contrary to our expectations, spectra at high energies can be analyzed with simple spectroscopic models in reduced dimension space.² These models are described by resonance Hamiltonians which have regular localized eigenfunctions, and this explains the regular patterns frequently found in vibrationally excited spectra.

Semiclassical approximations seem to provide a satisfactory theory for the localization of the wave functions. Particularly, it has been found that periodic orbits may be used as diagnostic tools for the localization in quantum mechanics.³ Regular wave functions have recognizable nodal structures which follow the patterns of periodic orbits.³ For high vibrational excitations of particular interest are those periodic orbits which emerge from saddle node (SN) bifurcations. These periodic orbits appear suddenly in phase space as pairs of one stable and one unstable family. This is important, since the emergence of a SN bifurcation signals the existence of stable domains in phase space embedded in a usually chaotic region. The correspondence of stable periodic orbits to quantum eigenfunctions⁴ dictates quantum mechanical localization as well.

In double well potentials, periodic orbits which connect the two minima are mainly associated with SN bifurcations. We have shown this for bound⁵,⁶ and unbound⁷ molecular systems. A recent example with a spectroscopic signature for the SN states is the HCP molecule. Dispersed fluorescence and stimulated emission pumping vibrational-rotational spectroscopy⁸,⁹ of the bending mode has shown that the rotational constants are different for the normal mode type bending states (states associated with the minimum of the potential) and the isomerizing bending states. Although ab initio calculations for the ground electronic state of HCP predict a saddle point for the CPH conformation and not a minimum, it has been demonstrated that the vibrational states which lead loosely speaking to isomerization of the hydrogen atom from the carbon to phosphorus side are associated with SN periodic orbits.¹⁰-¹² The van der Waals system Ar₃ is another example which can show inversion of the axial atom with respect to the A−A bond. In this case, the transition state is a collinear configuration with the axial A atom sitting in the middle of the A−A bond. An example is H₂⁺, for which it has been shown that localized isomerizing states exist and are marked by similar types of periodic orbit named “horseshoe.”¹³

Homonuclear triatomic molecules, A₃, can also show inversion of the axial atom with respect to the A−A bond. In this case, the transition state is a collinear configuration with the axial A atom sitting in the middle of the A−A bond. An example is H₂⁺, for which it has been shown that localized isomerizing states exist and are marked by similar types of periodic orbit named “horseshoe.”¹³

The van der Waals system Ar₃ is another example which can show inversion of the axial Ar atom. The weak forces among the atoms dictate that the molecule executes floppy irregular motions. Early studies on this system revealed that the trajectories even close to the minimum have positive Lyapunov exponents.¹⁴,¹⁵ However, more recent classical mechanical studies¹⁶,¹⁷ have shown a nonstatistical inversion dynamics in spite of the fact that the phase space is dominated by chaotic trajectories above the inversion threshold.
Vibrational quantum mechanical calculations for the rotationless system have recently been presented by Wright and Hutson.\textsuperscript{19} What is surprising in these calculations is the regularity and localization of a few eigenfunctions above the barrier of inversion found among irregular eigenstates with no recognizable nodal patterns.

In this article we want to investigate more thoroughly the inversion dynamics and spectroscopy of the van der Waals system, $\text{Ar}_3$. Thus, we apply the periodic orbit method (POM) introduced before.\textsuperscript{1} Families of periodic orbits which originate from the saddle point of the potential function as well as saddle node bifurcations are located to explore the structure of phase space in regions where inversion takes place. These periodic orbits are then used to guide wave packets which are propagated by solving the time dependent Schrödinger equation. The important role of the initial phase of the wave functions (assigned by the momenta of POs) results in completely different spectra produced at high energies, where wave packets with the same amplitudes but different phases serve to excite the molecule in different modes.

We apply a new algorithm and recent ideas on high order finite difference method\textsuperscript{19} to obtain the solutions of the Schrödinger equation which are then compared with the results of fast Fourier pseudospectral calculations. The curved shape of the potential function leads the finite difference method to a superior position since it allows us to choose the grid points in an energetically optimum way and to apply the appropriate boundary conditions. Details of the finite difference methods are presented in the companion paper.\textsuperscript{20}

### II. NUMERICAL DETAILS

Both classical and quantum calculations are performed for $C_{2v}$ geometries of the three argon atoms using the Hamiltonian:

$$H = \frac{p_1^2}{2\mu_1} + \frac{p_2^2}{2\mu_2} + V(x_1, x_2).$$

\(x_1\) is the position of the axial argon atom along a perpendicular axis to the middle of the bond length, \(x_2\), of the other two argon atoms. \(\mu_1\) is the reduced mass of the axial argon atom with respect to \(\text{Ar}_2\) and \(\mu_2\) the reduced mass of \(\text{Ar}_2\). The potential function, \(V(x_1, x_2)\), is determined from the sum of the three \(\text{Ar}\text{–Ar}\) interactions. The latter are described by the empirical potential of Aziz and Slaman.\textsuperscript{21}

The same potential has been used by Dumont and Jain\textsuperscript{16} in a classical statistical study of the inversion dynamics. It supports two symmetric minima accessible through the inversion process. The minima are at \((x_1, x_2) = (\pm 6.15, 7.099) a_0\), the energy of which is taken to be equal to zero. The saddle point between these two minima has the collinear geometry of \((x_1, x_2) = (0.0, 14.19) a_0\), and energy 140.38 K above the minimum. The energies are measured in Kelvin.\textsuperscript{16} The dissociation limit to $\text{Ar} + \text{Ar}_2$ is 286.415 K. In Fig. 1 we show contour plots of the potential function covering the energy range between 50 and 300 K. In the insert the coordinates \(x_1\) and \(x_2\) are defined.

Methods for locating periodic orbits have been described before.\textsuperscript{22} Usually, a quasi-Newton method is employed to find the proper initial conditions for closing the trajectory. However, we are interested in locating families of periodic orbits for a range of energies. Thus, continuation methods are equally important.\textsuperscript{23} Through continuation of the principal families, i.e., families which emerge from the stationary points of the potential, we find bifurcations, and gradually unravel the structure of phase space for a domain of total energies. The stability properties of each periodic orbit, i.e., the behavior of the surrounding trajectories with time, are then examined by calculating the eigenvalues of the monodromy matrix.\textsuperscript{24,25}

Spectra and quantum mechanical wave functions are calculated by solving the time dependent Schrödinger equation using the Fourier pseudospectral (PS) method\textsuperscript{26} and a fast and numerically robust variable order finite difference (FD) method. Using recurrence relations for the Lagrange interpolation polynomials a general algorithm for computing any derivative of a function at arbitrary points and at any order of approximation have been presented by Fornberg.\textsuperscript{19,27} This allows us to check systematically the convergence of the spectra by increasing the order of approximation of the second derivatives. It can be shown that FD methods at the infinity order of approximation are equivalent to spectral methods. However, the desired accuracy is achieved for finite orders and this makes FD methods competitive to pseudospectral techniques. As the number of degrees of freedom increases the flexibility of choosing the grid points according to physical criteria makes FD methods superior to pseudospectral techniques.\textsuperscript{20} This is demonstrated even for the present 2D system for which rectangular grids, usually employed in fast Fourier transform methods, will lead to an inefficient configuration space sampling.

Some ways to optimize grids with FFT algorithms have been proposed\textsuperscript{28} but they are less general and not as easy to handle as a FD procedure. Finite differences not only offer flexibility in grid sampling, a property which is shared with
the discrete variable representation (DVR) pseudospectral methods, but also result in having a smaller number of non-zero Hamiltonian matrix elements than DVR. This is also in the spirit of other local and semilocal methods such as the distributed approximated functionals (DAF). Numerical details of the implementation of FD method in Ar are given in the next section.

III. RESULTS AND DISCUSSION

A way to represent families of periodic orbits as the total energy or other control variables change are via continuation/bifurcations (C/B) diagrams. These are plots of the initial conditions of the periodic orbits or their periods as functions of the total energy. Generally, C/B diagrams reveal the stable and unstable regions of phase space, and thus, they provide global information about the dynamics of the molecule. Their importance in molecular systems stems in the expected correspondence among stable and short period periodic orbits and quantum mechanical eigenfunctions.

Continuation/bifurcation diagrams are constructed for each stationary point of the potential function. The existence of the principal families of POs which originate from the stationary points are guaranteed by Weinstein and Moser theorems. Since here we are interested in the inversion dynamics of Ar, we discuss the C/B diagram of the saddle point.

There is one principal family which emerges from the saddle point. In Fig. 2 we plot a projection of the continuation/bifurcation diagram, the initial $x_1$ coordinate of each located periodic orbit versus the total energy. Continuous lines denote stable POs and dashed lines unstable POs. The periodic orbits of the principal family correspond to the symmetric stretch of the three atoms in collinear configuration. The principal family is denoted by $S$ in Fig. 2 and is initially unstable in the direction of $x_1$ axis. Interestingly enough, this family turns to stable POs about 10 K above the saddle point. At the critical energy where the $S$ turns from unstable to stable two new unstable families the $(S1A, S1B)$ are born. The stability island which is formed around the stable periodic orbits makes the isomerizing chaotic trajectories to be trapped around this region of phase space for a long time, something which is manifested in the inversion dynamics with the deviations from the statistical behavior.

In the diagram of Fig. 2 we can see the bifurcation of other families as well as the change of $S$ back to unstable POs at energy 390 K. Plots of representative POs are shown in Fig. 3 and initial conditions for one periodic orbit of each family are stored in Table I. It is interesting to note the simultaneous bifurcation of four new families, $S3$. The $S3A$ and $S3C$ POs have the same projection on the $(x_1, x_2)$ plane but they have a reflection symmetry ($p_{1,2} \rightarrow -p_{1,2}$) when they are projected on a coordinate-momentum plane.

The other class of POs with physical interest is the one which emerges from saddle node bifurcations and a few of them are shown in Fig. 2. We use the symbols $I0, I1, I2$, etc. to denote their association with the inversion. Indeed, the saddle node POs are those which connect the two minima and the symmetric ones can easily be found. They appear always with two branches, one stable and one unstable. The stable one may turn to unstable shortly after its generation.
and that depends on the particular system. The real value of the eigenvalue $\lambda$ of the monodromy matrix given in Table I reveals that the $I$ type P0s are mainly unstable.

To estimate the extension of the stable region around stable periodic orbits in Fig. 4 we plot Poincaré surfaces of sections, one with the $x_2 = 14.1865 a_0$ and one with $x_1 = 0 a_0$ and at energy of 192.4 K. It is interesting to note that the $S$ periodic orbits have a quite extended stable region (192.4 K), one on a $S$ type, $(x_{10}, x_{20}, p_{10}, p_{20}) = (0.0, 14.9094, 0.0, 2.6473)$ and $(\alpha_1, \alpha_2) = (0.37378, 0.37178)$. The second PO is of $I1A$ type with $(x_{10}, x_{20}, p_{10}, p_{20}) = (0.0, 14.9094, 3.0572, 0.0)$ and the same widths as the $S$ type. The average energy of the wave packets is 209.53 K.

The Fourier transforms of the autocorrelation functions, $I(E) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \exp(iEt/\hbar) \phi(x,0)\phi(x,t)dt$, are shown in Fig. 5 for the $S$ [Fig. 5(a)] and $I1A$ [Fig. 5(b)] POs, respectively. These markedly different spectra are the result of two excitations with initial Gaussians having the same center in configuration space and widths but differing in their initial phases because of the different momenta of periodic orbits.

Superimposed in Fig. 5(a) we show the calculated spectra using the Fourier pseudospectral method and a variable order FD method ($M = 5$, where the order $M$ is defined from the $N = 2M + 1$ number of grid points used in the centered equi-spaced grid approximation of the second derivatives). The two spectra are practically indistinguishable. We used the same grid spacing and ranges in configuration space for both methods but we generated an optimized grid set in the FD scheme, by selecting those grid points with potential energy below a cutoff value, $V_c = 400$ K. This amounts into reducing the number of grid points from 32 768 in the Fourier PS case (rectangular grid) to 13 338 points, which together with the use of the local approximation allows a reduction in time by a factor of 3. The calculations were done

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with and without absorbing boundary conditions and we obtained the same results. This is a consequence of the localization of the wave packet.

We use the spectral method 35 to filter out the eigenfunctions of the most intense peaks in the spectrum of Fig. 5(a). Although spectral methods are not as accurate as filter diagonalization techniques,36,37 for the present study where we seek a qualitative accuracy, these results are adequate. The progression of the five major lines are assigned to \((0,n)S\) states which are found to be regular and well localized in the region of the transition state as can be seen in Fig. 6. The label \(S\) is used to denote their association to the \(S\) periodic orbits. We note that the ground \((0,0)S\) state shows some probability amplitude along the reaction path, which we do not see for the excited states. We attribute this to the chaotic region of phase space with which the wave function overlaps at these energies (156.5 K).

The progressions between two successive major lines in the spectrum of Fig. 5(a) with decreasing intensities are due to wave functions of inversion type. In Fig. 7 we present the \((14,0)I\) and \((16,1)I\) states. Superimposed is an \(I0\) periodic orbit. Thus, the initial wave packet with a phase along the \(S\) periodic orbit excites not only symmetric stretch states but also the inversion states.

Contrary to that, filtering the eigenfunctions which correspond to the most intense peaks of the spectrum in Fig. 5(b) we find only isomerizing type wave functions (Fig. 8).
The saddle node periodic orbits of the /2 family seem to match very well with the (31,0), and (32,0) eigenstates.

Comparison with the 3D calculations of Wright and Hutson shows that similar eigenfunctions are obtained for the T-shaped inversion dynamics. The localization of states in the region of the transition state does not alter our conclusions extracted from the T-shaped inversion dynamics.

IV. SUMMARY AND CONCLUSIONS

In the past years several triatomic molecules have been studied within a program which involves the construction of C/B diagrams of the main families of periodic orbits and then the quantum mechanical study of the molecule for the comparison of PO results with the wave functions at particular energies. The periodic orbit method (POM) reveals the dynamical characteristics which are preserved in the quantum world. At high excitation energies localized regular states which correspond to saddle node periodic orbits are now well established.

This program applied to the inversion dynamics of the van der Waals system of Ar3 surprised us by showing stable periodic orbits at the region of the transition state (collinear geometries). Thus, regular eigenfunctions localized at the same region in configuration space are extracted by filtering a wave packet propagated in time. The most interesting, however, is the production of spectra distinctly different by monitoring the phase of the initial wave packet. It has been shown that wave packets launched onto orthogonal type periodic orbits, S and I, overlap with different type eigenfunctions, the symmetric stretches which inhibit the inversion process and those which promote the inversion process, respectively. This picture remains even when the third degree of freedom is included as recent calculations have shown.

We understand that experimentally it is difficult to study the spectroscopy of Ar3. However, there is a rich spectroscopy for H2+ species for which similar type saddle node periodic orbits have been located. We hope that the present results will stimulate further studies in this system, although we anticipate that the simplicity found in the weakly bound Ar3, which has a significantly less dense spectrum, can not be achieved.

In the present study we were able to further test a new high order finite difference method for solving the time dependent Schrödinger equation. We demonstrated that although pseudospectral methods based on FFT are fast and quite accurate for 2D systems, FD methods may give equivalent accuracies and even become faster because of the freedom in selecting the grid points. The complex configuration space of Ar3 makes the FD method more appropriate than the FFT one.

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