

Periodic orbits and bifurcation diagrams of acetylene/vinylidene revisited

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Transitions from normal-mode to local-mode states in the two bending oscillations of acetylene observed in spectroscopic studies, as well as the existence of localized vibrational states in vinylidene above the isomerization barrier to acetylene, are examined by constructing continuation/bifurcation diagrams of periodic orbits on a global potential-energy surface. The principal families of periodic orbits, which provide a faithful representation of the overtone vibrational states, show pitchfork bifurcations for the asymmetric stretch and the two bending families of acetylene, the fingerprints of the normal- to local-mode transitions, whereas for vinylidene most of the principal families of periodic orbits remain stable above the isomerization potential barrier, thus supporting the existence of localized vinylidene states. © 2003 American Institute of Physics.

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I. INTRODUCTION

Bifurcation phenomena¹ are interesting and revealing of the nonlinear mechanical behavior of a system. Bifurcations observed in the spectroscopy of molecules make these phenomena even more exciting, since they establish a correspondence between the quantum and classical world. In the last years, we have been studying vibrationally highly excited molecules in their isomerization and dissociation thresholds, and found saddle-node bifurcations to play a dominant role for the reaction.²⁻⁵ At lower energies the normal modes of the molecules may show another type of elementary bifurcation (pitchfork) by turning to local-mode vibrations.⁶⁻⁸

A molecule that has kept the interest of spectroscopists for decades is acetylene^{9,10} and particularly the problem of the isomerization of acetylene to vinylidene.¹¹ Contrary to acetylene, for which numerous spectroscopic studies exist, its isomer vinylidene has not been identified unequivocally, although its existence is strongly supported by theoretical calculations.¹²⁻¹⁸ The recent full dimensional (six) quantum-mechanical calculations of Zou and Bowman¹² for this four atom system reveal the difficulties in obtaining accurate eigenfunctions and eigenenergies at high vibrational states. Most of the quantum-mechanical investigations in the past were restricted into the planar configurations of the molecule with four or five degrees of freedom,^{15,16} and only recently Zou and Bowman¹³ extended these calculations at such energies where isomerization of acetylene could be studied. In this work the authors use a new full dimensional potential-energy surface^{17,18} (PES), which predicts a smaller barrier to isomerization than an older version produced by Carter *et al.*^{19,20} Isomerization rates have also been calculated by *ab initio* molecular dynamics¹⁴ supporting a long living vinylidene.

The most recent work concerning the spectroscopy of acetylene is that of Jacobson *et al.*,^{9,10,21} who studied dis-

persed fluorescence spectra at the energy region of 15 000 cm^{-1} . These excited states are close to the vinylidene minimum. By fitting the spectroscopically assigned levels of the *trans* and *cis* bending modes to an effective Hamiltonian, Jacobson *et al.* were able to show normal- to local-mode transitions. In a companion paper a semiclassical analysis was presented for this two-dimensional effective Hamiltonian.²² Although, stretching normal- to local-mode transitions are known,⁶ and the asymmetric stretch of acetylene does show such a transition, it was rather surprising to find a similar bifurcation phenomenon for the bending modes. Specifically, the *trans* bending normal mode exhibits a local one, whereas the *cis* bending normal mode turns to a counter-rotation for the two hydrogen atoms,^{21,22} i.e., the two hydrogen atoms executing rotations around the CC bond in opposite directions.

Acetylene is a good example to demonstrate the difficulties, both theoretical and experimental, one encounters in studying vibrationally highly excited polyatomic molecules. Most importantly, this work unveils the nonlinear dynamics of the molecule, which are manifested in its spectrum by observing the change of a complex spectrum to a simple one as energy increases or it may show bifurcations such as the transitions from normal to local modes.^{21,22} On the other hand, it is at this energy regime where we expect classical and semiclassical mechanics to approximate the dynamics of the molecule satisfactorily. Indeed, extended research has shown the predictive power of classical nonlinear mechanics.^{23,24} In particular, the principal families of periodic orbits (PO's) which correspond to the normal modes of the molecule and start from the minimum of the potential are faithful representations of the overtone states. The bifurcations of these families signal the appearance of new quantum states. Classical and semiclassical mechanics remain vital approximations to elucidate the dynamics of a molecule at very high excitations where elementary reactions such as isomer-

ization or dissociation occur.^{3–5} To explore molecular dynamics at such energies hundreds of eigenfunctions must be calculated, if that is possible, plotted, and assigned, a very tedious task indeed for a six degrees of freedom system. Tools to extract the dynamics of the molecule are needed and classical mechanics play a crucial role in this case. Periodic in time solutions of the classical equation of motions provide a systematic way to classify the types of motion in the molecule.

We have presented a periodic orbit analysis for both acetylene and vinylidene²⁵ in the past by using the global six-dimensional potential-energy surface of Carter *et al.*²⁰ and for energies up to 4.5 eV. In this work we did predict the normal- to local-mode transitions of the asymmetric stretch and *trans* bending, but since we were mainly interested in the planar motions of the acetylene, at that time, we did not locate the counter-rotation periodic orbits of the hydrogen atoms emerging from the *cis* bending normal mode. Furthermore, we predicted stable principal families of periodic orbits for vinylidene. No full dimensional quantum-mechanical results were available, and definitely, they were not easily accessible at high-energy regions.

In the light of the new spectroscopic and theoretical results for acetylene/vinylidene, we believe that a periodic orbit analysis of the PES used by Zou and Bowman is appropriate. This full degrees of freedom classical study will complement the recent quantum and semiclassical calculations.^{12,21,22} A second goal for this work is to compare the continuation/bifurcation (*C/B*) diagrams obtained with the two versions of the global potential function. Taking into account that the PES are continuously improved, it is necessary to know if the main dynamical characteristics of the system, as are portrayed in the *C/B* diagrams, do not change. In such a case we establish structural stability for the molecule.

II. THEORETICAL AND COMPUTATIONAL METHODS

The technical part of our methods to locate and continue with respect to the total energy or period the periodic orbits for a N degrees of freedom Hamiltonian system and the stability analysis of periodic orbits (PO's) have been described extensively in the past.^{2,26} However, for the sake of completeness of the paper we summarize the steps which are taken to compute periodic solutions of Hamilton equations.

The art of locating periodic orbits is greatly facilitated by the knowledge of Hamiltonian bifurcation theory. The fundamentals of this theory as well as computational techniques are introduced in Refs. 27 and 28. The first step is to find one PO for each family. Existence theorems dictate approximate initial conditions for these periodic orbits. For instance, from such theorems^{29,30} we know that around equilibrium points of the potential function periodic orbits exist and these families are named principal or main. After locating the PO we carry out linear stability analysis by computing the Monodromy matrix and we find its eigenvalues. These eigenvalues ($2N$ in number) tell us if the periodic orbit is stable or unstable and the directions in phase space where instability is developed. To locate new members of the family we vary in small intervals the parameter of the system

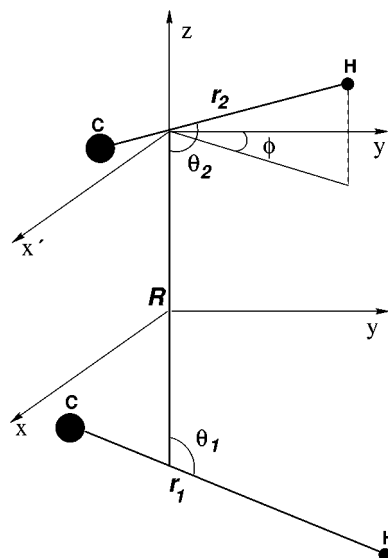


FIG. 1. The Cartesian (xyz) and diatom-diatom coordinate systems used for acetylene. $x'y'$ is the plane where the dihedral angle ϕ is defined.

to larger or smaller values. Furthermore, we can predict the bifurcation critical values of the varying parameter and the new PO's which emanate from those points. All elementary bifurcations¹ have been identified in molecular Hamiltonians. The simplest and most generic bifurcation is the saddle-node, i.e., the abrupt appearance of periodic orbits showing no connection to previous families. Such bifurcations have extensively been studied by us in association to molecular spectroscopy.^{2–4} Plotting the initial conditions and period of PO's as functions of the varying parameter consists the continuation/bifurcation diagram.

The potential-energy function that we use is a refinement of the Carter *et al.*²⁰ potential based on the accurate *ab initio* calculations of Stanton and Gauss.³¹ The more pronounced difference between the two functions is the height of the barrier of isomerization of vinylidene to acetylene. In the old version is 0.373 eV and in the new 0.107 eV. The energy of vinylidene minimum has also changed. Relative to the acetylene minimum, it is 1.735 eV in the Carter *et al.* potential and 1.991 eV in the new function. The location of PO's has been done in a Cartesian coordinate system with 12 degrees of freedom. The momenta are adjusted to ensure zero total angular momentum. However, to plot the trajectories we use the diatom-diatom (CH–CH) coordinate system shown in Fig. 1. We employ Newton-Raphson multiple shooting techniques to find the periodic orbits.³² We proceed in the next section with the results and discussion.

III. RESULTS AND DISCUSSION

In Fig. 2 we plot the frequencies of acetylene obtained from the periods of PO's ($\omega = 2\pi\hbar/T$) for an energy range of about 2 eV. This is a projection of the continuation/bifurcation diagram. It differs from what was shown in our first paper, where we plotted the conjugate momentum of one hydrogen position as a function of the total energy. Any projection of the *C/B* diagram conveys the same information with respect to the bifurcating families and the stability of

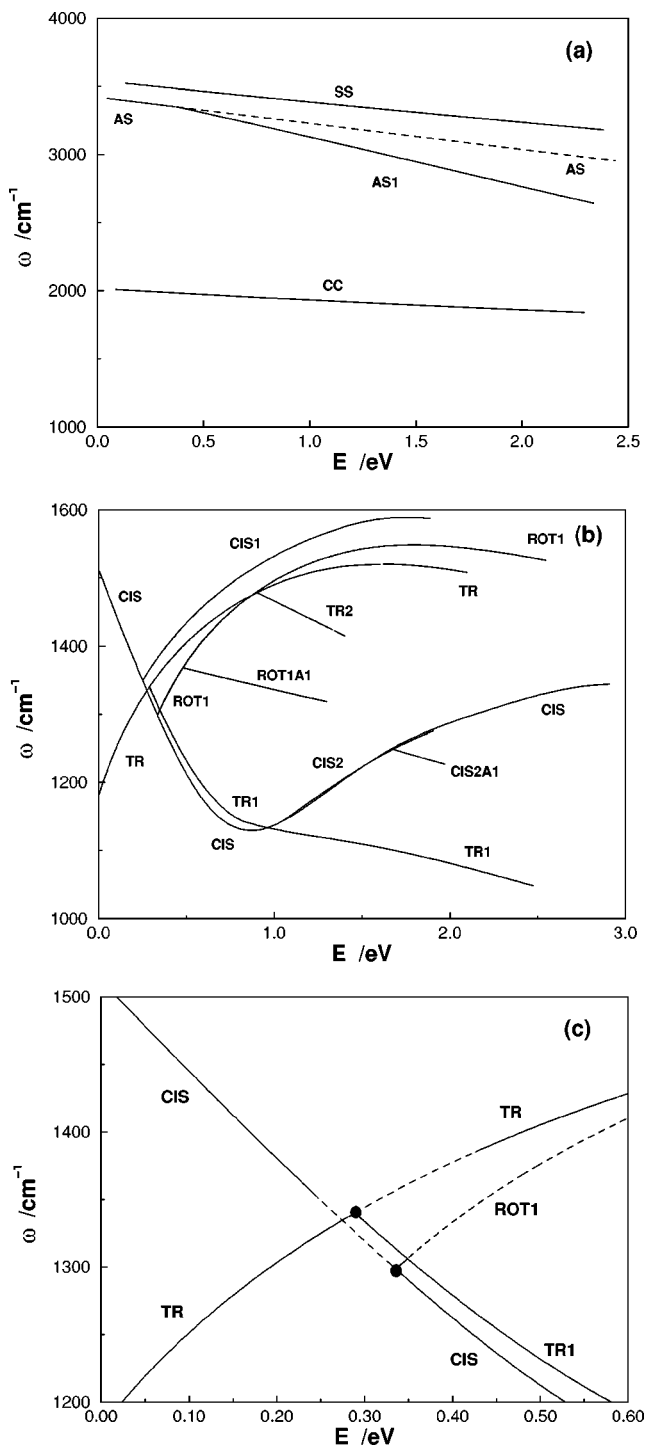


FIG. 2. Continuation/bifurcation diagrams of acetylene; (a) The symmetric stretch (SS), the asymmetric stretch (AS), and the CC bond stretch; (b) the two bending *trans* (TR) and *cis* (CIS) modes; and (c) magnification of the *trans* and *cis* bending bifurcation diagram. For the plots in (a) and (c) continuous lines mean stable PO's and dashed lines unstable.

periodic orbits. However, frequencies are useful when we compare PO's with experimental or calculated spectra. Simple semiclassical arguments correspond these frequencies to the energy differences between adjacent energy levels in overtone progressions.

In Fig. 2(a) we plot the three stretch families and in Fig. 2(b) the two bending modes, each of them doubly degener-

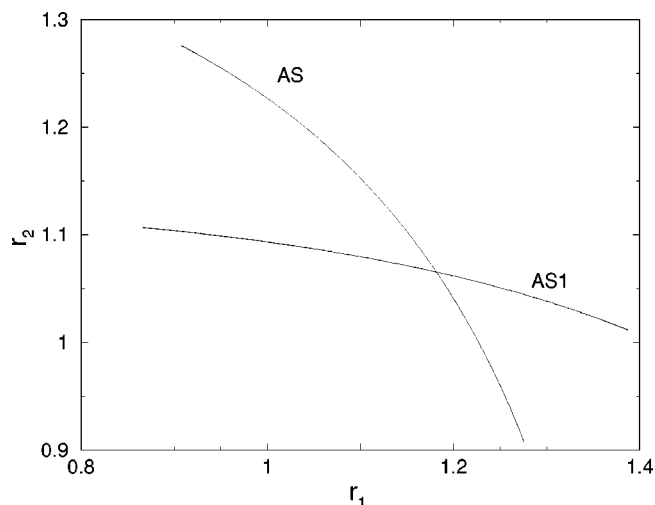


FIG. 3. Periodic orbits for the asymmetric stretch family and its bifurcation of acetylene.

ate. The total energy is with respect to the minimum of acetylene and the origin is not translated by adding the zero-point energy (ZPE) of acetylene (0.7236 eV). The symmetric stretch (SS) and the CC bond stretch remain stable for the total-energy interval studied. The asymmetric stretch (AS) becomes singly unstable at 0.372 eV (measured from the absolute minimum of the potential) giving birth to two new periodic orbits with the same period as the asymmetric stretch. This is a typical pitchfork bifurcation and signals the appearance of local type motions. As we can see in Fig. 2(a) the mother family continues singly unstable at higher energies. The normal- to local-mode transition was predicted by Kellman and co-workers^{33,34} and Child and co-workers³⁵ using model potentials of acetylene. Typical periodic orbits are depicted in Fig. 3 in the (r_1, r_2) plane. The bifurcating AS1 PO's run almost parallel to the CH bonds and mark the doublet quantum states associated with the normal- to local-mode transitions.⁷

Figure 2(b) contains the bifurcation diagram of the *cis* and *trans* bending families. For comparison with the work of Jacobson *et al.*,²¹ where the even quantum number bending states are assigned, we have double the frequencies. The *trans* family shows a pitchfork bifurcation at the energy of 0.289 eV with the new families staying for most energies stable. The TR becomes stable again at 0.42 eV. Projections of typical PO's are shown in Fig. 4(a). We project the trajectory in the (θ_1, θ_2) plane where the bifurcating TR1 PO's remain almost parallel to one of the angles, thus showing their local character. The stability of the bifurcating periodic orbits (TR1) means that the region of phase space around them is less chaotic, and this explains the remark of Jacobson *et al.*²¹ that the spectrum becomes less complex at higher energies.

For the *cis* bending principal family we initially located an out-of-plane periodic orbit at the energy 0.253 eV, CIS1. However, the counter-rotation periodic orbits emerge at the energy of 0.335 eV, ROT1. Plots of representative PO's from this family are shown in Fig. 4(b). We can see that the dihedral angle ϕ varies from zero to 2π . Figure 2(c) is the mag-

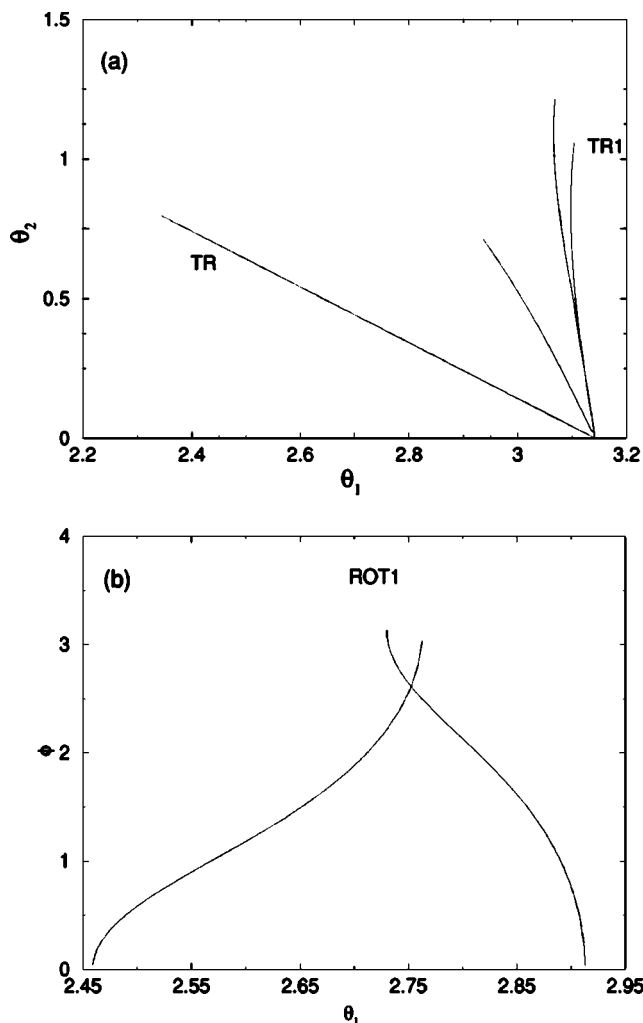


FIG. 4. Periodic orbits for (a) *trans* and local mode bifurcating families, and (b) counter-rotation bifurcation family of acetylene.

nification of that part of Fig. 2(b) which contains the bifurcations of *trans* and *cis* counter-rotation. We see that the CIS family has turned to unstable at 0.252 eV and it becomes stable again at the bifurcation energy of ROT1. The counter-rotation PO's are unstable.

Comparing Fig. 2(c) with the two-dimensional quantum results shown in Fig. 7 of the Jacobson *et al.*²¹ paper, we see that the bifurcation analysis of periodic orbits on the global potential-energy surface correctly predicts that, first, the bifurcation of the *trans* mode (TR1) occurs at a lower energy than the bifurcation of the *cis* mode (ROT1). Second, the counter-rotation has a negative anharmonicity and the TR1 a positive anharmonicity. However, while the continuation lines cross in Fig. 2(c), the quantum-mechanical results show an avoided crossing. Even correcting with the ZPE it is not possible to bring classical and quantum pictures into agreement, which means that the global potential function does not predict the bending energy levels accurately at this region of the spectrum.

Figure 5 depicts the *C/B* diagram of vinylidene. Again, the energies are with respect to the absolute minimum and we have not taken into account the ZPE of vinylidene (0.7058 eV). The six normal-mode principal families are pre-

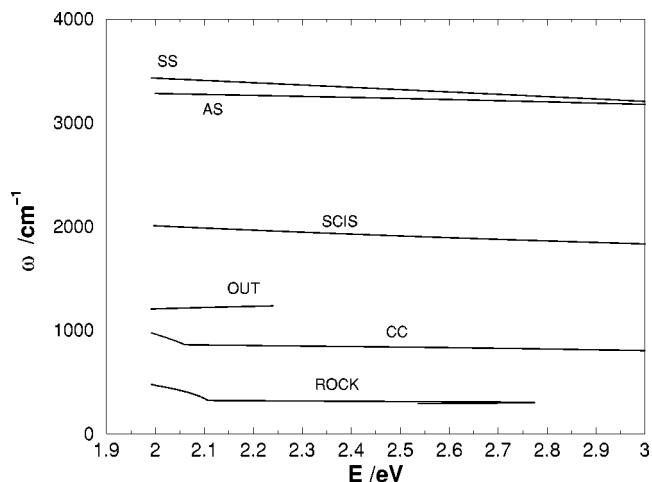


FIG. 5. Continuation/bifurcation diagram of vinylidene. See text for their stability.

sented. All of them show several alterations in their stability with the increase of energy. What is most important to point out is the energy range for which they keep their initial stability. The symmetric stretch (SS) remains stable up to 3.542 eV after which it turns to complex unstable. The asymmetric stretch (AS) at the energy 2.349 eV develops a pitchfork bifurcation, the CC stretch after an early period doubling bifurcation turns to stable again up to 2.339 eV. The scissors mode (SCIS) remains stable up to 2.801 eV, whereas the rock mode stays stable up to 2.102 eV, and the out-of-plane mode (OUT) is stable up to 2.240 eV. The above underlines the fact that all principal families are stable at least up to the isomerization barrier which is located at 2.098 eV.

To investigate the stability of the trajectories around the periodic orbits of vinylidene we have calculated the classical autocorrelation function by propagating in time wave packets represented by 5000 trajectories at the range of 2.110 ± 0.1 eV.³⁶ The results are shown in Fig. 6. The peaks in the autocorrelation functions denote recurrences of the nearby trajectories to their starting points, and thus they remain close to periodic orbits for some time. That behavior reflects the stability or small instability of the phase space region. We remark from Fig. 6 that the most stable modes are the stretch ones and the least the out-of-plane motion. However, comparing these plots with Fig. 12 in Ref. 25, we see that in the new potential the recurrences do not persist as long as in the old potential, which means that the vinylidene region of phase space is less stable in the new potential. This is not surprising, since the barrier has been lowered in the new version of the function.

The frequencies of the periodic orbits close to the minimum of vinylidene approximate the harmonic normal-mode frequencies. These can be compared with the frequencies obtained from the *ab initio* calculations.^{14,17} Differences up to 650 cm^{-1} are observed, which demonstrates that the global PES does not represent the vinylidene minimum accurately. On the other hand, comparing the *C/B* diagrams obtained with the two versions of the potential for acetylene/vinylidene we find no significant qualitative differences, although we do notice changes in the stability of PO's. For

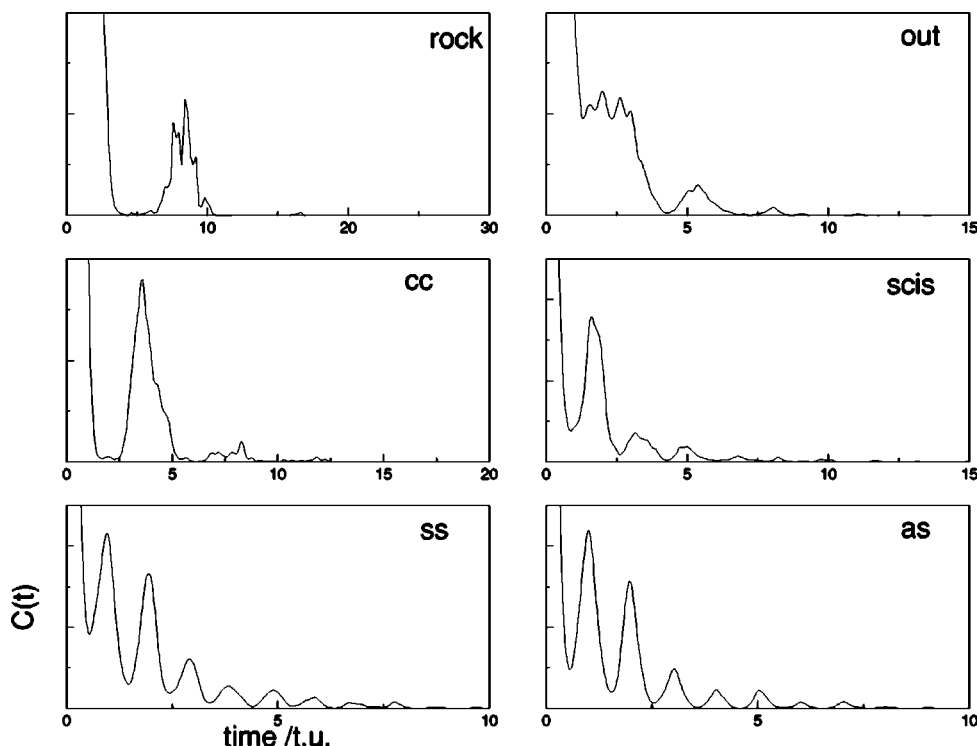


FIG. 6. Classical autocorrelation functions for vinylidene. Wave packets are represented by 5000 trajectories and centered on periodic orbits with energy 2.110 eV and spread 0.2 eV. One time unit = 1.018×10^{-14} s.

example, in vinylidene the CC stretch mode is more stable in the old version than in the new, something which could be explained by the lower isomerization barrier.

Finally, we comment on the relation of the principal families of PO's and their corresponding quantum states with respect to the isomerization process. As we can see from the *C/B* diagrams, these families are extended above the barrier of isomerization, and therefore represent localized states either in acetylene or vinylidene minimum. Isomerizing states are usually assigned with periodic orbits originated from saddle-node bifurcations. Such PO's, that connect the two minima, were shown in our first paper²⁵ and they are located above the isomerization barrier. Saddle-node bifurcations below the barrier are also expected, and they were found in other molecules.⁴ We have not searched for them in the present study.

IV. SUMMARY

The beautiful spectroscopic work of Jacobson *et al.*^{9,10,21} published recently in a series of papers revealed bifurcations for the bending modes of acetylene, manifesting themselves as transitions from normal to local modes for the *trans* bending and from normal to counter-rotation of the two hydrogen atoms in *cis* bending. These bifurcations are predicted by the periodic orbits analysis on global full dimensional potential-energy surfaces. The same type of analysis confirms the conclusions for localized vinylidene states in the recent full dimensional quantum-mechanical calculations of Zou and Bowman.¹² This conclusion is also supported by the classical autocorrelation functions. However, comparison with the ex-

perimental results and *ab initio* calculations elevates the inadequacy of the global PES to reproduce the spectroscopy of acetylene/vinylidene at the excited vibrational levels. This became apparent to Zou and Bowman who have just published an *ab initio* PES.³⁷ Accurate six dimensional quantum mechanical calculations but only for acetylene have recently been reported by Guo and co-workers.³⁸

Our second goal in this study was to see how the *C/B* diagrams change with the refinement of the analytical potential function, a very common task but tedious in molecular dynamics. The qualitative agreement between the old and new bifurcation diagrams, as well as with the effective Hamiltonian of Jacobson *et al.*,^{21,22} underlines the structural stability of acetylene/vinylidene. The latter means that we find no qualitative differences in the dynamics of the molecule by introducing perturbations in the original Hamiltonian. Differences in the critical energies where bifurcations occur of course are expected.

In this study the location of periodic orbits and the construction of continuation/bifurcation diagrams were carried out in the 12 degrees of freedom Cartesian coordinate space and with zero total angular momentum. We believe that a similar type of work can be done to larger polyatomic molecules where nonlinear effects are expected to appear at lower excitation energies. This is important because full dimensional quantum-mechanical calculations are currently not possible, and isomerization reactions have been experimentally studied for large molecules.³⁹ That will allow us to investigate further the bifurcations related to elementary reactions.

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