A Periodic Orbit Approach to Spectroscopy and Dynamics of SO_2 : $\tilde{\mathrm{C}}\,^1B_2 \rightarrow \tilde{\mathrm{X}}\,^1A_1$

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Abstract

Dispersed Fluorescence spectra of SO_2 are simulated by semiclassical mechanics using a spectroscopic potential for the excited state and an empirical and an ab initio surface for the ground electronic state. The initial vibrational states on the excited electronic state are calculated quantum mechanically, a coherent state representation of which provides the initial distributions in the classical calculations. We find two classes of vibrational wavefunctions in the upper surface with characteristic localization properties, which can be associated with periodic orbits emerging from saddle-node bifurcations above the potential barrier. The dynamics on the ground surface, induced from the spectroscopic transitions, are analyzed with periodic orbits, and the semiclassical Gutzwiller's formula. This type of analysis elucidates the regularity of the observed spectra.

1 Introduction

The rapid developments of the theory of chaos in the last two decades,[1] and mainly their applications in molecular dynamics,[2] have triggered parallel research in experimental vibrational spectroscopy.[3] The detection of chaotic behavior in vibrationally excited small polyatomic systems has been the driving force for a detailed spectroscopic study of a number of molecules, such as acetylene,[4] NO_2,[5] Na_3,[6,7] HCN,[8] O_3,[9,10] CS_2,[11] and SO_2.[12,13] However, in spite of all this work, there is still no satisfactory definition of quantum chaos, since the concepts and quantities used to define chaos in classical mechanics are not immediately transferable in quantum mechanics, the theory which describes molecules. Nevertheless, some criteria related with the morphology of eigenfunctions and the distribution of the eigenenergies have been proposed.[1]

There are two reasons for which molecules are considered as interesting species in studies of quantum chaos. First, they are amenable to experimental observations, and second, since localized states may occur at high vibrational levels in conjunction to the chaotic diffused states, the study of highly excited molecules is important for state specific chemistry.

The investigations have revealed that a typical molecular system can show three different dynamical regimes for its bound states as energy increases. At low energies the dynamics is regular in both the classical and the quantum mechanical description. At intermediate energies the phase space is occupied by resonances, where regular and chaotic trajectories coexist. At this energy range the quantum eigenfunctions remain regular and localized in the resonance zones. Finally, at high energies most of the phase space is occupied by chaotic trajectories and the quantum eigenfunctions are spread all over the available configuration space, but may show localization along unstable periodic orbits in a varying degree. The energy at which we observe the transition from one regime to the other varies from molecule to molecule, and it may happen that the molecule dissociates before extended chaotic regions occur. For example, in van der Waals systems and floppy molecules chaotic motion appears very early, even below the zero point energy.[14,15] On the other hand, conventional molecules like HCN and H_2O show regular behavior even above the threshold of dissociation.[16,17]

SO_2 is an important molecule for atmospheric and combustion chemistry. Furthermore, for some time now, it has also attracted the interest of workers wishing to investigate molecular chaos. Using an empirical potential function for the ground electronic state, Farantos and Murrell[18] found that the onset of chaotic dynamics is at about 1.5 eV above the minimum. Frederick, McClelland, and Brumer[19] showed that even at 1.9 eV a substantial region of phase space is occupied by regular trajectories. Experimental results have recently been obtained by Yamanouchi et al.,[12,13] who have studied the vibrational spectroscopy of this molecule using Dispersed Fluorescence (DF), and Stimulated Emission Pumping (SEP) techniques.[20]

Based on the work of Brand et al.[21] who observed DF spectra by exciting the $\tilde{\mathrm{C}}\,^1B_2 \to \tilde{\mathrm{X}}\,^1A_1$ band, Yamanouchi et al. recorded transitions to the ground state up to 2.68 eV from eight single rovibronic levels of the $\tilde{\mathrm{C}}\,^1B_2$ state. Specifically, the (0,0,0), (0,1,0), (0,2,0), (0,0,2), (1,0,0), (1,1,0), (1,2,2), and (3,1,0) levels of the $\tilde{\mathrm{C}}\,^1B_2$ electronic state were used, with the integers (ν_1, ν_2, ν_3) corresponding to the symmetric stretch, bending, and antisymmetric stretch modes respectively. From the 1388 observed transitions 484 vibrational levels distributed between 0.53 and 2.68 eV were assigned with three normal mode quantum numbers. The excitation was mainly in the symmetric stretch and bend modes. Thus, the spectrum of SO_2 was characterized as regular for an energy range up to the half of dissociation. However, for energies above 2.65 eV the spectroscopists observed an increasing number of resonances, an indication of the onset of chaos.

The early appearance of chaotic dynamics found in the classical trajectory calculations[18] is not surprising, as it is now known that quantum mechanics remains stable for higher energies than classical mechanics. Even in the energy regime where the classical phase space is predominantly chaotic, the quantum eigenfunctions may be localized along periodic orbits.[22–24] It is, however, interesting to investigate the cause of quantum localization.

Sulfur dioxide is a promising molecule for the experimental investigation of the transition from regular to resonance and chaotic states, and it deserves further theoretical study. In this article, we present a phase space structure analysis of the ground electronic state, and we use it to extract the dynamics from the observed DF spectra. The latter are simulated by the classical survival probability function.[7,25]

The initial distributions are obtained from the quantum mechanical vibrational states of the $\tilde{\mathrm{C}}\,^1B_2$ surface.

We use 3-D empirical potential functions for both the ground and excited electronic states, but these results are compared with calculations on an ab initio ground state surface as well. The peculiar morphology of the vibrational wavefunctions of the $\tilde{\mathrm{C}}\,^1B_2$ surface is explained by their localization along periodic orbits which are generated from *saddle-node* bifurcations. The latter it turns out to appear systematically above potential barriers and their importance in molecular dynamics is discussed.

2 Computational Methods

The classical mechanical investigation is carried out by solving Hamilton's equations and variational equations of motion. Let $\vec{x}$ be the column vector of the generalized coordinates, $\vec{q}$, and their conjugate momenta, $\vec{p}$, which describes the state of a system with N degrees of freedom;

$$\vec{x} = (q_1, ..., q_N, p_1, ..., p_N)^+, \tag{1}$$

where $+$ denotes the transpose matrix. The equations of motion are written,

$$\dot{\vec{x}}\,(t) = J\frac{\partial H(\vec{x})}{\partial \vec{x}} = J\nabla H(\vec{x}), \tag{2}$$

where $H(\vec{x})$ is the Hamiltonian of the system, $\cdot = d/dt$, and

$$J = \begin{pmatrix} 0_N & I_N \\ -I_N & 0_N \end{pmatrix}, \tag{3}$$

a symplectic matrix, which satisfies the relations

$$J^{-1} = -J, \quad \text{and} \quad J^2 = -I_{2N}. \tag{4}$$

0_N and I_N are the zero and unit $N \times N$ matrices respectively.

The main topological characteristics of phase space are traced by first locating the equilibrium points of the dynamical system, $\dot{\vec{x}}= 0$, or

$$\nabla H(\vec{x}) = 0. \tag{5}$$

Second, the classical objects of higher dimensionality and importance are periodic orbits;

$$\vec{x}(t) = \vec{x}(t+T), \tag{6}$$

where T is the period.

According to the Weinstein and Moser theorems[26,27] from the stable equilibrium points at least N families of periodic orbits emanate which are called *principals*. From saddle points unstable families of periodic orbits emerge. By following the evolution of principal families with the total energy, we can locate new families of periodic orbits with the same or multiple periods which bifurcate from the parent ones. The theory of bifurcations of periodic orbits as well as their stability analysis is well developed, and the representation of the results are commonly given by a bifurcation diagram;[28–30] the plot of the initial conditions of periodic orbits with the total energy or any other parameter used.

The stability of periodic orbits is examined by calculating the eigenvalues of the monodromy matrix, which is obtained by integrating the variational equations over one period of the periodic orbit.[29,30] If all eigenvalues appear as complex conjugate pairs with norm equal to one, then the periodic orbit is stable. If one or two pairs of eigenvalues are real reciprocal numbers the periodic orbit is called single or double unstable respectively. If there are complex conjugate eigenvalues with norm different than one the periodic orbit is then complex unstable. Applications of constructing bifurcation diagrams of periodic orbits pertinent to molecular systems have been given before.[31,32]

In these studies we have found that an important kind of bifurcations is that of *saddle-node* type.[29] We can consider a saddle-node bifurcation as the coalescence of two families of periodic orbits at some particular value of the total energy. For 2-D systems, at the bifurcation point two families of periodic orbits are generated, one stable and one unstable, and all eigenvalues of the monodromy matrix are equal to one with degenerate eigenvectors. Since they appear suddenly, they have also been named "periodic orbits out of nowhere".[33]

By studying a number of molecular potentials we have found, that saddle-node bifurcations emerge systematically above the saddle points of the potential functions, but such bifurcations are a more general phenomenon in non linear systems and can appear with any type of potential function.[34] Saddle-node bifurcations are of extreme importance in molecular dynamics, since the stable branch creates a region in phase space with stable trajectories even when the system is highly unstable at lower energies.

Although the periodic orbits and their stability analysis do not provide a complete description of the structure of phase space (tori,[35] reduced dimension tori,[7] stable and unstable manifolds of unstable periodic orbits[36] are also important objects), nevertheless, they give the portrait of the main characteristics of the phase space.

The aim of this paper is to provide an interpretation of the experimentally observed DF and SEP spectra of Yamanouchi et al.,[13] and to extract the dynamics of the molecule. The method we use to achieve this goal is to calculate the classical survival probability function

$$C(t) = \int \rho[\vec{q}(0), \vec{p}(0)]\rho[\vec{q}(t), \vec{p}(t)]d\vec{q}d\vec{p}, \tag{7}$$

where $\rho[\vec{q}(0), \vec{p}(0)]$ describes the distribution of the initial conditions of a batch of trajectories. This function is usually the Wigner or a coherent state representation of the initial quantum state in the DF or SEP spectrum. According to semiclassical arguments for the time evolution of the distribution ρ, we solve Hamilton's equations of motion to evaluate $\rho[\vec{q}(t), \vec{p}(t)]$, and Eq. (7) can be considered as the autocorrelation function of ρ. The Fourier transform of $C(t)$ is the classical analogue of the spectrum.

To simulate the experimental spectra we need both potential functions, for the excited, $\tilde{\mathrm{C}}\,^1B_2$, and the ground, $\tilde{\mathrm{X}}\,^1A_1$, electronic states, and their description is given in the next section. We assume a constant dipole moment hypersurface. The excited surface provides the initial vibrational states and distribution functions, whereas the dynamics is carried out on the ground electronic state.

Thus, $\rho(0)$ is obtained by taking a coherent state representation of the vibrational eigenfunctions, $\psi(\vec{q})$, in the excited electronic state,

$$\phi[\vec{q}_0, \vec{p}_0] = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \psi(\vec{q})\, \Pi_{i=1}^{N} \exp[-\sigma_i^2(q_i - q_{0i})^2 + ip_{0i}(q_i - q_{0i})/\hbar]\, dq_1 dq_2 ... dq_N, \tag{8}$$

which is expressed on a grid of points and the integral (8) is obtained by a Fast Fourier Transform algorithm. Initial conditions for the trajectories are then sampled with a Monte Carlo Metropolis method[37] according to the probability distribution function,

$$\rho = |\phi|^2. \tag{9}$$

Further details are given in the following section.

For an explicit connection of periodic orbits with the fluctuating part of the density of states we apply Gutzwiller's trace formula.[1]

3 Results

3.1 The saddle-node vibrational states of $\tilde{C}\,^1B_2$ surface

The spectroscopy of the $\tilde{X}^1A_1 \rightarrow \tilde{C}^1B_2$ transition has been the subject of several investigations, because of the perplexing features of the antisymmetric mode.[38] The (0,0,0) - (0,0,2) transition is anomalously intense, more than the (0,0,0) - (0,0,0) band, and also the term value of 562 cm^{-1} is considered small compared to the harmonic value, $\omega_3 = 623$ cm^{-1}. Furthermore, the energy difference of adjacent levels increases with the excitation which suggests positive anharmonicities.

The above observations have led to the conclusion that the potential should be a double well function. Hoy and Brand[38] have obtained a potential function for the excited $\tilde{C}\,^1B_2$ surface with a double minimum in the antisymmetric stretching normal coordinate, q_3, and strong anharmonic coupling of q_3 with the symmetric stretch normal coordinate, q_1, which has a harmonic frequency of $\omega_1 = 928$ cm^{-1}. The spectroscopic analysis has shown that the bending mode, q_2, with a harmonic frequency of $\omega_2 = 384$ cm^{-1}, does not strongly interact with the other degrees of freedom, thus, a 2-D model hamiltonian for the stretching modes, and a harmonic approximation for the bending is a satisfactory representation of the potential energy surface for the energies of interest. The vibrational hamiltonian used is;

$$\begin{gathered} H = \frac{1}{2}\omega_1(q_1^2+p_1^2) + \frac{1}{2}\omega_2(q_2^2+p_2^2) + \frac{1}{2}\omega_3(q_3^2+p_3^2) + \\ \frac{1}{6}f_{111}q_1^3 + \frac{1}{2}f_{133}q_1q_3^2 + \frac{1}{24}f_{1111}q_1^4 + \frac{1}{4}f_{1133}q_1^2q_3^2 + \frac{1}{24}f_{3333}q_3^4 + \\ \frac{B\omega_3\exp(\rho)}{\exp(\rho)-\rho-1}\exp\{-[\exp(\rho)-\rho-1]q_3^2/2B\} + C\exp[-D_1(q_1-q_{10})^2 - D_3(q_3-q_{30})^2]. \end{gathered} \tag{10}$$

The parameters are given in ref. [38]. The last Gaussian term has been added by us to eliminate a deep hole in the potential, which however, does not alter the fitted region of the minima and saddle points. The parameters of the Gaussian term are; $C = 15$ eV, $D_1 = 0.025$, and $D_3 = 0.095$, $q_{10} = 22.195$, and $q_{30} = 0.0$.

The potential function is shown in Fig. 1. The saddle point is at $(q_1, q_3) = (0, 0)$ and 0.0175 eV above the minima, which are located at $(q_1, q_3) = (0.32, \pm 1.419)$.

Because of the existence of the low potential barrier the dynamics is chaotic for energies below and just above the saddle point. However, as we have emphasized before, above the saddle point we expect the creation of saddle-node bifurcations. This has a dramatic effect in the case of SO_2.

Indeed, at 0.0558 eV above the minimum, a saddle-node bifurcation emanates which creates a stable family of periodic orbits with periods of about 100 fs. At the energy of 0.27 eV another saddle-node bifurcation with the stable periodic orbits having periods of about 60 fs was located.[39]

We have found more bifurcations,[39] but it turns out that the above two have the largest influence in the phase space. We have named these families S1 and S3 and representative orbits are shown in Fig. 2. Figs. 3 and 4 show Poincaré surfaces of sections at different energies. These graphs, obtained by running one chaotic trajectory, reveal how the genesis of the stable periodic orbits originating from saddle-node bifurcations influence the phase space.

The extended regular regions in phase space created by the saddle-node bifurcations mark the quantum eigenfunctions which are localized in the same regions, and they have similar morphology as the periodic orbits S1 and S3. In Fig. 5 we show some of the eigenfunctions which clearly reveal the influence of periodic orbits. They have been obtained by solving the time dependent Schrödinger equation and using an initial Gaussian wave packet centered on the appropriate periodic orbit.[39] These wavefunctions are used to assign initial conditions to the trajectories run in the ground electronic surface by taking a coherent state representation. Before analyzing the time evolution of these distributions in the classical mechanical approximation, we first investigate the structure of phase space in the ground electronic state.

3.2 The phase space structure of $\tilde{\mathbf{X}}\,^1\mathbf{A}_1$ surface

The empirical potential function which we use is that of Sorbie-Murrell.[40] The surface predicts several stationary points. Two minima which correspond to OSO (absolute) and SOO (relative) configurations. A third minimum with elongated SO and OO bond lengths which was also found, is rather an artifact of the potential function. The two lower minima are located at -11.2228 eV and with geometry $(r_1, r_2, \phi) =$ (1.4308 Å, 1.4308 Å, 119.3^0), and -10.2933 eV at $(r_1, r_2, \phi) =$ (2.64 Å, 1.69 Å, 22.86^0) respectively. r_1 and r_2 are the two SO bond lengths, and ϕ the angle between them. There are two saddle points of interest, the one for linearizing the molecule, OSO, -9.4861 eV, at (1.40 Å, 1.40 Å, 180^0), and the barrier of isomerization between the two minima, -7.9921 eV, at (1.85 Å, 1.85 Å, 88.4^0). This potential is the only one available which describes the molecule in full configuration space. Other analytical potentials have been published, but they were fitted to reproduce the first few vibrational levels.[41]

In the present work, we also use the ab initio potential function of Weis et al.[42] which is valid in the range of (1.2, 1.7) Å for the r_1 and r_2, and in the range of $(90^0, 150^0)$ for the angle ϕ. In Fig. 6 we compare the ab initio surface (dotted lines) with that of Murrell et al.[40] (solid lines). We can see that there is good agreement with respect to the symmetric stretch mode up to about 3.5 eV, but the ab initio potential rises faster in the bending coordinate. In the following section we compare the results obtained by both surfaces, the empirical and ab initio one.

In Fig. 7 the bifurcation diagram of families of periodic orbits is shown projected in the (E, ϕ) plane. From the absolute minimum of the potential the three principals families emanate and they are labeled as SS, AS, and B, and correspond to the symmetric stretch, antisymmetric stretch, and bend modes respectively. Continuous lines mark stable periodic orbits, dotted lines correspond to single unstable periodic orbits, and open circles to double unstable periodic orbits. Families which bifurcate are denoted by numerals, whereas the different branches are labeled with the letters A and B.

We have found a saddle-node bifurcation above the lowest potential barrier of the linearization of the molecule and the stable and unstable families are denoted by

R1A, and R1B respectively. These periodic orbits connect the two symmetrically located minima, (OSO), of the potential function. Representative periodic orbits of the families are shown in Fig. 8, and their initial conditions are tabulated in Table I.

The following remarks can be extracted from the bifurcation diagram. The AS principal family remains *stable* for all energies studied. The bending family becomes single unstable at 0.8 eV above the minimum and for the short energy interval of 0.2 eV. The bifurcating periodic orbits are of double period (B1A and B1B). The SS and B families become single unstable at about 1.7 eV above the minimum. Note, the interesting bifurcation of the SS family which shows a "bubble". A similar type of bifurcation has been observed in model potentials.[43]

We have found for other systems[44] that excitation of the bending mode leads to chaotic behavior at lower energies than excitation of the stretching modes. From Fig. 7 we see that although the B family shows an early transition to instability this is for a short range of energies. Extended chaos is introduced when the bending periodic orbits become single unstable just below the first barrier of linearization, OSO, whereas the symmetric stretch family turns to single unstable with a period doubling at about the same energy. The latter reveals a strong coupling between the symmetric stretch and bend coordinates. However, we may conclude that overall the phase space maintains a regular region for energies up to 1.8 eV, in accordance to Frederick et al.[18,19]

It is important to emphasize that even above the barrier of linearization the appearance of the saddle-node bifurcations create a regular region around the stable periodic orbits. The analysis of power spectra of batches of trajectories selected around the stable branch of R1 shows, that the regularity increases with the energy.

Furthermore, we point out, that the R1 periodic orbits are different from the bending ones. The B family continues for energies above the barrier, as we can see from the bifurcation diagram (Fig. 7), and changes from double to single unstable again. Plots of the periodic orbits of this family by increasing the energy reveal how the bending trajectories are folded and avoid to overcome the barrier of linearization. No complex unstable family of periodic orbits was found in the present work of SO_2.

3.3 Classical mechanical spectra of $\tilde{\mathbf{C}}\,{}^1B_2 \rightarrow \tilde{\mathbf{X}}\,{}^1A_1$ transition

We now proceed to calculate the classical mechanical spectra which originate from the initial states C: (0,0,0), (1,0,0), (0,0,1), and (0,0,2). Initial conditions for batches of 1000 trajectories were selected from the distributions ρ obtained from the coherent state representation of the above states, and with probability larger than 40%. Fig. 9 shows projections of ρ s, on the (r_1, r_2) bond lengths plane, in the ground potential energy surface. The dots represent initial points for the trajectories and the nodal pattern of the wavefunctions is reflected in these distributions. Runs with batches of 2000 trajectories were also performed for a few distributions with probabilities larger than 20%. Apart from small differences in the intensities of the lines no other significant deviations were found.

The survival probability function, $C(t)$, for the ground vibrational initial state C(0,0,0) is first calculated. The spectrum, obtained by Fourier transforming the $C(t)$, is compared with the experimental one in Fig. 10. The autocorrelation function is marked by progressions of the bending mode, whereas the spectrum shows stacks of three peaks. Under low resolution we could assign the clumps as progressions of the bending mode. Comparison with the experimental spectrum shows an agreement as far as the position of the peaks is concerned. However, there are differences in the intensities of the individual lines, as well as in the width of the total spectrum. The latter disagreement is more severe, since it indicates deviations of the potential function used from the real one. We analyze this further at the end of this section.

Yamanouchi et al.[12,13] have assigned most of the observed lines in this spectrum with excitations in the symmetric stretch and bending modes. Indeed, analysis of the trajectories which contribute to the survival probability function are of this type. The peak in the energy of the initial distribution is at about 1 eV, which corresponds to a region of phase space well characterized by quasiperiodic trajectories.

We have also examined the spectra produced from the other initial distributions shown in Fig. 9, and we found that the general characteristics of the C(0,0,0) spectrum described above remain, and this is in agreement with the spectroscopic results. The energies sampled in the ground electronic surface using the above distributions are in the regular region of phase space, and thus, the regularity of the spectra is explained. Since, the classical survival probability function does not reproduce the intensities, we did not examine spectra with other experimentally studied initial states.

We showed before, that in the C state the vibrational eigenfunctions have a distinguishable morphology because of their localization in the regions of phase space marked by the S1 or S3 saddle-node bifurcations. The question thus arises, what spectra will such states give?

We have examined the spectra of two distributions obtained from the wavefunctions shown in Fig. 5 and which are assigned as $C(0,0,3)$ and $C(0,0,3)'$. The first is influenced by the S1 family and the second by the S3 family of periodic orbits, and the distributions projected on the ground potential surface are shown in Fig. 11. Comparison of the survival probability functions and their spectra, (Fig. 12), shows mainly differences in the intensities of the lines but similar positions. For aesthetic reasons we plot the spectra for positive and negative frequencies. The $C(0,0,3)$ initial state gives intense bending lines, whereas the $C(0,0,3)'$ distribution shows doublets. The average excitation energy is about 1.7 eV and the spectra can be characterized as regular.

The main difference in the two states when they are projected on the ground electronic surface is that, the (0,0,3) distribution samples regions with high energy in both the antisymmetric and symmetric modes, whereas the $(0,0,3)'$ state covers regions with high energy in the symmetric stretch mode.

Calculations of the spectra with the ab initio potential surface of Weis et al.[42] have been carried out for the C(0,0,0) initial state. The larger steepness of the ab initio potential (Fig. 6) results in a faster initial decrease of the survival probability function, and thus, in a broader spectrum, in accordance to Heller's time dependent description of the photoabsorption spectroscopy.[45] In Fig. 13 we compare the two spectra produced from the C(0,0,0) initial state in the ab initio (a) and empirical potential (b). Although the positions of the lines are not altered, the difference in the width of the spectra can be seen.

3.4 Semiclassical Density of States

A connection of the periodic orbits with the fluctuating part of the density of states can be obtained from Gutzwiller's trace formula,[1]

$$D(E) = \sum_n \delta(E - E_n) = D_{av}(E) + N(E),$$

where

$$N(E) = Re \sum_{po} \frac{T_{po}}{\pi\hbar} \sum_{j=1}^{\infty} \frac{\exp[ij(S_{po}/\hbar - \mu_{po}\pi/2)]}{[det(M_{po}^j - 1)]^{1/2}}. \tag{11}$$

$D(E)$ is the density of states at energy E, and $D_{av}(E)$ the average density of states. The sums in Eq. 11 are over all periodic orbits with period T_{po}, action S_{po}, and for an infinite number of loops j. μ_{po} is the Maslov index (number of turning points) and M_{po}^j is the stability matrix which describes the results of the transverse displacements off the periodic orbit after j loops. The determinant in Eq. (11) can be obtained from the eigenvalues of the monodromy matrix,

$$det(M_{po}^j - 1) = \prod_{i=1}^{2(N-1)} (\lambda_{po}^j(i) - 1), \tag{12}$$

where $\lambda_{po}^j(i)$ is the jth power of the ith eigenvalue (a complex or real number) of the monodromy matrix which corresponds to a perpendicular direction of the periodic orbit. The above quantities are computed as functions of the total energy during the periodic orbit analysis.

According to Eq. (11) the calculation of the density of states requires a summation over all periodic orbits and for an infinite number of loops of each periodic orbit. However, it turns out[46] that a low resolution spectrum can be obtained by including a finite number of periodic orbits.

Another point of concern is the convergence of the trace formula with respect to j. This is facilitated by multiplying the terms in the summation formula with the smoothing function[1,47]

$$f(E) = \exp\left[-\frac{\gamma j T_{po}(E)}{\hbar}\right], \tag{13}$$

where $\gamma > 0$ is a decay parameter.

Fig. 14a shows the fluctuating part of the semiclassical density of states using the symmetric stretch and bend principal families of periodic orbits, SS, and B, shown in Fig. 7, and for an energy range up to 2 eV above the minimum of the potential. The vertical lines at the top of the figure denote the quantum levels assigned by Yamanouchi et al.[13] They are mainly progressions in the symmetric stretch $(\nu_1, 0, 0)$, $(\nu_1 = 1 - 15)$, bend $(0, \nu_2, 0)$, $(\nu_2 = 1 - 5)$ and $(\nu_1, \nu_2, 0)$, $(\nu_2 = 1, 2)$. Spectroscopically, more levels have been located among those which we show.

Fig. 14b shows the $N(E)$ function calculated using all principal families as well as the B1A bifurcating family. The period of the antisymmetric stretch (AS) periodic orbit is very close to the symmetric stretch one and therefore peaks which correspond to the antisymmetric stretch levels are not resolved.

We have also computed the $N(E)$ function using the ab initio potential energy surface and the principal families of periodic orbits. The AS family remains stable for all the energy range studied, as was found for the empirical potential function. The SS becomes single unstable at -9.22 eV in the ab initio potential, whereas the B family becomes single unstable at -8.71 eV, and then turns to stable again at -8.65 eV, and single unstable at -8.40 eV. No significant differences are observed in the fluctuating part of the density of states given by the empirical and ab initio surfaces.

If we exclude the first few peaks of $N(E)$ for which a one to one correspondence to the observed levels can be established, the rest of the them provide a low resolution picture to the experimental spectrum, allowing to see the progressions in the symmetric stretch and bend lines. This result also came from the classical survival probability function. However, the trace formula provides a direct connection between periodic orbits and observed quantum levels.

4 Discussion and Conclusions

There is no doubt that the detailed spectroscopic results of Yamanouchi et al.[13] require a detailed quantum mechanical calculation for both, the potential functions and the vibrational energy levels. This task can be accomplished with the present computer technology, but it will be a difficult problem if we ask for an ab initio potential valid for energies up to dissociation, and the vibrational levels covering a large range of frequencies.

Classical mechanics applied through periodic orbits analysis and the calculation of survival probability functions, as we have presented it here and in our previous work on HCN,[25] offers a qualitative explanation of the underline dynamics in a recorded DF spectrum, as well as semi-quantitative information when low resolution characteristics of the spectra are demanded.

The classical dynamical study has revealed some important features. First, in spite of the existence of chaotic regions of phase space embedded in regular regions, the classical spectrum depicts the regular components, and results in a regular spectrum. Second, we may predict from the phase space structure analysis, that regularity will remain at even higher energies of excitation. Assuming localization of eigenfunctions along the periodic orbits, we must reach the energy of the potential barrier before change from stable to single or double unstable periodic orbits occur, and that will happen mainly by exciting the symmetric stretch and bend modes.

Even above the barrier of linearization of the molecule we can see that regular regions exist because of the saddle-node bifurcations of periodic orbits R1A (Fig. 7). The latter guarantees that localized eigenfunctions will exist at these energies and they may give intense lines in the spectrum if they are appropriately excited.

For SO_2 the saddle-node type states seem to play an interesting role. As we have shown the appearance of the small barrier in the C-state implies the generation of the saddle-node type periodic orbits along which the vibrational eigenfunctions are localized. Projections of the distributions obtained from the eigenfunctions on the ground electronic surface tell us that we can excite vibrational states with most of the energy in the antisymmetric mode (those influenced by S1-type periodic orbits) or states with symmetric stretch excitation (S3-type). This is predicted from plots of the type shown in Fig. 9 and becomes more apparent for higher levels (Fig. 5). It would be interesting if these conclusions can be tested by spectroscopic experiments.

Making predictions for vibrationally highly excited molecules one has first to secure a valid potential function. We have tried to test our results on the empirical ground potential surface by using the ab initio potential of Weis et al.[42] Apparently, the Murrell-Sorbie type function is too soft with respect to the angle variations, which results in a narrower spectrum. Unfortunately, the ab initio surface is valid for configurations with energies up to about 2 eV above the minimum, and does not reproduce any other stationary points of the hypersurface. Without doubt the barriers of linearization and isomerization of SO_2 as predicted by the Murrell-Sorbie surface will change when more accurate results will be available. However, we believe that the main topological characteristics of phase space will remain. For example, the principal families of periodic orbits propagated above the barriers will remain but their stability may change. Also, we expect to find saddle-node bifurcations above the barriers creating stable regions in phase space. This belief is supported by studies with other molecular potentials. In the van der Waals system Ar-CO,[48] where the unassignable eigenfunctions dominate, the localization of a few of them was attributed to periodic orbits of saddle-node type. In the photodissociation processes of ozone[49] and CO_2[50,51] resonance states have been found which give some oscillatory structure in an otherwise broad spectrum. These resonances have been explained by periodic orbits.

Summarizing our results we can state that, the DF and SEP spectroscopy of SO_2 in the ground electronic state is regular and will remain regular at even higher excitation energies than those studied by Yamanouchi et al.[12,13] Resonances will be the interesting features of the spectra at high vibrational levels and their reproduction by quantum mechanical calculations will be a real test of the potential functions. Isomerizing type states, those localized along saddle-node periodic orbits, may be found above the barriers of the potential. Sometimes, these states may be identified from the energy difference of adjacent levels, which increases with the energy, as in the C state of SO_2, but this of course can not be generally true, since the behavior depends on the nonlinearities of the potential.

The periodic orbit analysis turns out to be a powerful method for analyzing the spectroscopy and dynamics of a molecule. Furthermore, it can provide guidance in the quantum mechanical calculations[39] or by using the semiclassical approximation of the density of states low resolution spectra can be accomplished.

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References

[1] M. C. Gutzwiller, 1990, *Chaos in Classical and Quantum Mechanics*, **1**, (Springer-Verlag).

[2] S. C. Farantos, 1992, In T. Bountis, editor, *Chaotic Dynamics: Theory and Practice*, (Plenum Co. Ltd.).

[3] K. Yamanouchi, S. Takeuchi, and S. Tsuchiya, 1989, *Prog. Theor. Phys.*, **98**,420.

[4] E. Abramson, R. W. Field, D. Imre, K. K. Innes, and J. L. Kinsey, 1985, *J. Chem. Phys.*, **83**, 453.

[5] H. Köppel, W. Domcke, and L. S. Cederbaum, 1984, *Advances in Chemical Physics*, **57**, (John Wiley and Sons, Inc.).

[6] M. Broyer, G. Delacretaz, G. Q. Ni, R. L. Whetten, J. P. Wolf, and L. Wöste, 1989, *J. Chem. Phys.*, **90**, 4620.

[7] J. M. Gomez Llorente and H. S. Taylor, 1989, *J. Chem. Phys.*, **91**, 953.

[8] X. Yang, C. A. Ragashi, and A. M. Wodtke, 1990, *J. Opt. Soc. Am. B*, **7**, 1835.

[9] D. E. Freeman, K. Yoshino, J. R. Esmond, and W. H. Parkinson, 1984, *Planet. Space Sci.*, **32**, 239.

[10] B. R. Johnson and J. L. Kinsey, 1989, *J. Chem. Phys.*, **91**, 7638.

[11] J. P. Pique, M. Joueux, J. Manners, and G. Sitja, 1991, *J. Chem. Phys.*, **95**, 8744.

[12] K. Yamanouchi, H. Yamada, and S. Tsuchiya, 1988, *J. Chem. Phys.*, **88**, 4664.

[13] K. Yamanouchi, S. Takeuchi, and S. Tsuchiya, 1990, *J. Chem. Phys.*, **92**, 4044.

[14] S. C. Farantos, and J. Tennyson, 1985, *J. Chem. Phys.*, **82**, 2163.

[15] S. C. Farantos, and J. Tennyson, 1986, *J. Chem. Phys.*, **84**, 6210.

[16] Z. Bacic and J. N. Light, 1989, In *Ann. Rev. Phys. Chem.*, **40**, 469.

[17] S. C. Farantos and M. Founargiotakis, 1990, *Chem. Phys.*, **142**, 345.

[18] S. C. Farantos, and J. N. Murrell, 1981, *Chem. Phys.*, **55**, 205.

[19] J. H. Frederick, G. M. McClelland, and P. Brumer, 1985, *J. Chem. Phys.*, **83**, 190.

[20] See the articles in issue, 1990, *J. Opt. Soc. Am. B*, **7**, 1802–1970.

[21] J. C. D. Brand, D. R. Humphrey, A.E Douglas, and I. Zanon, 1973, *Can. J. Phys.*, **51**, 530.

[22] E. Pollak and M. S. Child, 1981, *Chem. Phys.*, **60**, 23.

[23] E. Pollak, 1981, *Chem. Phys.*, **61**, 305.

[24] E. J. Heller, 1984, *Phys. Rev. Letters*, **53**, 1515.

[25] S. C. Farantos, J. M. Gomez Llorente, O. Hahn, and H. S. Taylor, 1990, *J. Chem. Phys.*, **93**, 76.

[26] A. Weinstein, 1973, *Inv. Math.*, **20**, 47.

[27] J. Moser, 1976, *Commun. Pure Appl. Math.*, **29**, 727.

[28] J. Guckenheimer, and P. Holmes, 1983, *Nonlinear Oscillations, Dynamical Systems, and Bifurcations of Vector Fields*, (Springer-Verlag, Berlin).

[29] R. Seydel, 1988, *From Equilibrium to Chaos: Practical bifurcation and stability analysis*, (Elsevier).

[30] E. Reithmeier, 1991, *Periodic Solutions of Nonlinear Dynamical Systems*, Lecture Notes in Mathematics, (Springer-Verlag).

[31] S. C. Farantos, 1992, In J. Broeckhove, editor, *Time Dependent Quantum Mechanics: Experiments and Theory*, (Plenum Co. Ltd).

[32] S. C. Farantos, and L. Zachilas, 1993, *Mol. Phys.*, **80**, 1499.

[33] J.-M. Mao and J. B. Delos, 1992, *Phys. Rev.*, **A45**, 1746.

[34] M. Founargiotakis, S. C. Farantos, G. Contopoulos, and C. Polymilis, 1989, *J. Chem. Phys.*, **91**, 1389.

[35] M. V. Berry, and M. Tabor, 1977, *Proc. Royal Soc. London A*, **356**, 375.

[36] R. Scharf and B. Sundaram, 1992, *Phys. Rev.*, **A45**, 3615.

[37] N. Metropolis, A. Rosenbluth, M. Rosenbluth, A. Teller, and E. Teller, 1953, *J. Chem. Phys.*, **21**, 1087.

[38] A. R. Hoy, and J. C. D. Brand, 1978, *Mol. Phys.*, **36**, 1409.

[39] S. C. Farantos, 1993, *Laser Chem.*, **13**, 87.

[40] J. N. Murrell, S. Carter, S. C. Farantos, P. Huxley, and A. J. C. Varandas, 1984, *Molecular Potential Energy Functions*, (Wiley and Sons).

[41] H. Wei and Jr. T. Carrington, 1992, *J. Chem. Phys.*, **97**, 3029.

[42] B. Weis, 1992, *University of Frankfurt, Main,*, PhD thesis.

[43] G. Contopoulos, 1983, *Physica D*, **8**, 142.

[44] S. C. Farantos, and J. Tennyson, 1987, In R. Lefebvre and S. Mukamel, editors, *Stochasticity and Intramolecular Redistribution of Energy*, 15, (D. Reidel, Dordrecht).

[45] E. J. Heller, 1981, *Acc. Chem. Res.*, **14**, 368.

[46] H. Friedrich and D. Wintgen, 1989, *Phys. Reports*, **183**, 37.

[47] M. V. Berry, and M. Tabor, 1976, *Proc. Royal Soc. London A*, **349**, 101, and E. Bogomolny, and C. Schmit, 1993, *Nonlinearity*, **6**, 523.

[48] L. Zachilas and S. C. Farantos, 1991, *Chem. Phys.*, **154**, 55.

[49] S. C. Farantos, 1992, *Chem. Phys.*, **159**, 329.

[50] K. C. Kulander, C. Cerjan, and A. E. Orel, 1991, *J. Chem. Phys.*, **94**, 2571.

[51] R. Schinke and V. Engel, 1990, *J. Chem. Phys.*, **93**, 3252.

TYPE	E (eV)	r_1	r_2	ϕ	p_{r_1}	p_{r_2}	p_ϕ	T (t.u.)	stabil.
B	-9.29164	1.43080	1.43080	2.78428	2.46154	2.46154	-1.28343	8.45989	DU
AS	-9.28973	1.56696	1.43080	2.02321	-3.18461	4.22755	0.05872	2.62058	S
SS	-9.28773	1.43080	1.43080	2.05059	5.02452	5.02452	0.42424	3.08967	DU
B1A	-9.29018	1.43080	1.43080	2.63225	3.74841	3.74841	0.39599	14.96032	S
B2A	-9.28791	1.43080	1.43080	2.91020	1.89303	1.89303	-0.97314	17.21090	U
SS1A	-9.28511	1.43080	1.43080	2.00932	4.82389	4.82389	-0.18070	6.18037	U
SS2A	-9.29401	1.41462	1.43080	2.05377	4.54666	5.40665	0.39826	3.09456	U
R1A	-8.45687	1.43080	1.43080	1.42016	1.40075	1.40075	2.73378	14.36437	S
R1B	-8.48091	1.43080	1.43080	2.95834	3.45251	3.45251	-1.97174	18.22514	U
R1A1A	-8.48217	1.47000	1.47000	1.57180	3.24537	3.24537	4.82978	15.32985	S
R1A1B	-8.47865	1.43080	1.43080	3.02437	2.25779	2.25779	-3.18539	15.33619	S
R1A2A	-7.37784	1.47000	1.47000	1.29457	2.53999	2.53999	3.56818	14.16217	U

TABLE I Initial conditions for representative periodic orbits. T is the period of periodic orbits in time units (1 t.u. = 1.018×10^{-14} s), S denotes stable periodic orbit, U single unstable, and DU double unstable periodic orbit. The bifurcations of the B family, B1 and B2, and of the SS family, SS1, occur when one pair of eigenvalues of the monodromy matrix is equal to -1. Thus, the periodic orbits of the B branches are the same with those of the A branches.

Figure Legends

1. Contours of the potential energy surface of the $\tilde{\mathrm{C}}\,^1B_2$ state of SO_2 in the symmetric (q_1) and antisymmetric stretch (q_3) normal coordinates. Contour energies are -0.01, 0.5, 1.0, 1.5, and 2.0 eV.

2. Representative periodic orbits generated from the saddle-node bifurcations S1 and S3. S1S and S3S are stable periodic orbits and the S3U unstable. The dotted line is the contour of the potential at the same energy.

3. Poincaré surfaces of sections obtained by integrating one chaotic trajectory and for different energies, ($q_3 = 0, p_3 > 0$). It shows the influence of the stable branch of the S1 saddle-node bifurcation in phase space.

4. As Fig. 3 but for higher energies. Note, the influence of the stable S3S family of periodic orbits in phase space.

5. Eigenfunctions localized in the regions of the S1 and S3 types periodic orbits. Wavefunctions with the same number of nodes are labeled with unprimed integers when they are associated with the S1 type periodic orbits, and with primed integers, when they are associated with the S3 type periodic orbits. For example the (0,0,5) state is on the left of the figure and $(0,0,5)'$ on the right. The integers correspond to the symmetric stretch, bending, and antisymmetric stretch modes respectively.

6. Comparison of the empirical potential of Murrell et al.[40] (solid lines) with the ab initio surface of Weis et al.[42] (dotted lines). The validity of the ab initio potential is for $1.2 < r_1, r_2 < 1.8$ Å and $70^0 < \phi < 130^0$. Distances in Å, and angles in rad.

7. Projection of the bifurcation diagram in (E, ϕ) plane showing the principals and saddle-node families of periodic orbits, and bifurcations of them. The symbols denote the symmetric stretch (SS), the antisymmetric stretch (AS), the bending (B), and the saddle-node families (R1). Continuous lines mark stable periodic orbits, dotted lines correspond to single unstable periodic orbits, and open circles to double unstable periodic orbits.

8. Representative periodic orbits projected in the (r_1, ϕ) plane. Their initial values are tabulated in Table I.

9. Distributions of the initial conditions of the trajectories which are used in the calculations of the classical survival probability functions, and projected on the ground state potential surface. Distances in Å.

10. Comparison of the experimental spectrum (a) of Yamanouchi et al.[13] with the theoretical one (b) for the C(0,0,0) initial state.

11. Projections of the initial distributions ρ obtained from the wavefunctions $C(0, 0, 3)$ and $C(0, 0, 3)'$.

12. The classical autocorrelation functions and their Fourier transforms obtained from the $C(0, 0, 3)$, and $C(0, 0, 3)'$ initial states. (1 t.u. $= 1.018 \times 10^{-14}$ s).

13. Comparison of the classical spectra of the $C(0, 0, 0)$ state produced with the ab initio surface (a), and the empirical potential (b).

14. The fluctuating part of the density of states for the ground electronic state of SO_2 calculated by Gutzwiller's semiclassical formula. $N(E)$ is produced from (a) the SS, and B principal families of periodic orbits, and (b) the SS, AS, B, and B1 families shown in Fig. 7. The vertical lines denote the experimentally assigned vibrational levels and correspond mainly to progressions of the $(\nu_1, 0, 0)$, $(\nu_1 = 1 - 15,)$, $(0, \nu_2, 0)$, $(\nu_2 = 1 - 5,)$, and $(\nu_1, \nu_2, 0)$, $(\nu_2 = 1, 2)$ levels.