Dynamical Interpretation of the Hartley-Absorption Oscillations in O_3

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The Fourier transform of the Hartley uv absorption spectrum in ozone is shown to have small recurrent features on time scales of typical molecular vibrations. These times are found to correspond closely to those of classical periodic or near-periodic orbits on a global excited-state potential-energy surface.

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The Hartley band in ozone ($1\,^1B_2 \leftarrow X\,^1A_1$ in C_{2v} symmetry) is the primary uv absorption and photodissociation channel above the $1\,^1B_2$ continuum threshold of 32200 cm^{-1}. This is an intense and broad band with small, unidentified oscillations, as shown in Fig. 1 in the absorption cross section measured at $T=195$ K by Freeman, Yoshino, Esmond, and Parkinson.[1] In attempting to understand the oscillations we have Fourier transformed the cross section to find small features occurring at times comparable to vibrational periods. These times can be identified with the periods of certain (sometimes unstable) classical trajectories on the $^1B_2$ potential surface of Sheppard and Walker[2] which return to the Franck-Condon region. This unexpected turn of events leads, with a certain amount of numerical effort, to a new level of understanding of the important classical dynamics in the energy range of the Hartley maximum (~39160 cm^{-1}). The vibrational-time assignments in the case of dissociating O_3 resemble the recent electronic-motion assignments of the quasi-Landau oscillations observed in magnetized Rydberg atoms,[3-11] as well as recent work concerned with near- and above-dissociation level structure in H_3^+.[12,13]

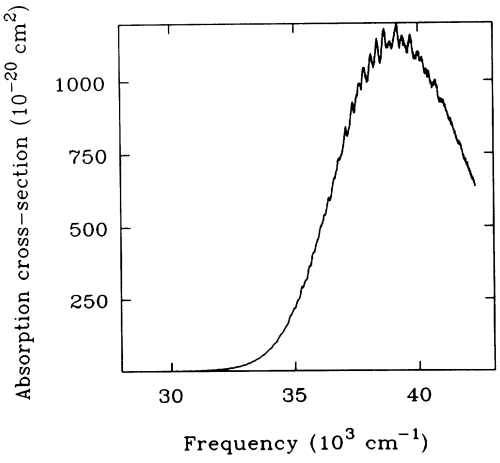

FIG. 1. Absorption cross section of ozone taken at $T=195$ K (from Ref. 1).

The O_3 measurements of Freeman *et al.*[1] cover the wavelength region 350–240 nm (28600–42269 cm^{-1}) with a total of over 132000 points. The greatest concentration of points is in the weak Huggins band (>315 nm), although the Huggins structure is invisible on the scale of Fig. 1. Other measurements of the uv cross section have recently been made,[14,15] motivated by the importance of ozone in atmospheric absorption and chemistry. For the present analysis, the data of Freeman *et al.*[1] are well suited because of the low temperature, detailed calibration, and high number of points.

Our analysis of the absorption cross section ϵ is based on its representation as a Fourier integral over the dipole-dipole autocorrelation function.[16] Inversely, the autocorrelation function can be expressed as an integral over ϵ,

$$\langle\Phi(0)\,|\,\Phi(t)\rangle \propto \int_{-\infty}^{+\infty} d\omega \exp(-i\omega t - iE_0 t/\hbar)\epsilon(\omega)/\omega\,. \tag{1}$$

Here E_0 is the energy of the initial vibration-rotation level $|\psi_0\rangle$ of the $X\,^1A_1$ state. The initial state is $|\Phi(0)\rangle = \boldsymbol{\mu}\cdot\mathbf{e}\,|\psi_0\rangle$, where $\boldsymbol{\mu}$ is the transition dipole moment operator and $\mathbf{e}$ is the appropriate polarization vector. At later times, the nonstationary $|\Phi(t)\rangle$ evolves under the $^1B_2$ nuclear Hamiltonian H, i.e., $|\Phi(t)\rangle = \exp(-iHt/\hbar)\,|\Phi(0)\rangle$.[16] Use of the experimental absorption cross section in Eq. (1)[5,17] gives an approximate autocorrelation function whose absolute value is displayed in close-up in Fig. 2. This function is normalized to unity at $t=0$ for convenience.

The decay of the initial peak within a few femtoseconds, responsible for the broad, continuumlike nature of the spectrum as seen under low resolution, occurs as the nuclear wave packet $\Phi(r_1,r_2,\theta,t)$ moves out of its original neighborhood in the configuration space of the two bond lengths r_1 and r_2 and the included angle θ. (Rotational degrees of freedom are unimportant on this time scale.) Figure 3 displays the $^1B_2$ potential surface of Sheppard and Walker[2] adapted from the earlier *ab initio* calculations of Hay, Pack, Walker, and Heller.[18] To indicate the approximate Franck-Condon region, the wave function $\psi_0(r_1,r_2,\theta)$ has been calculated variation-

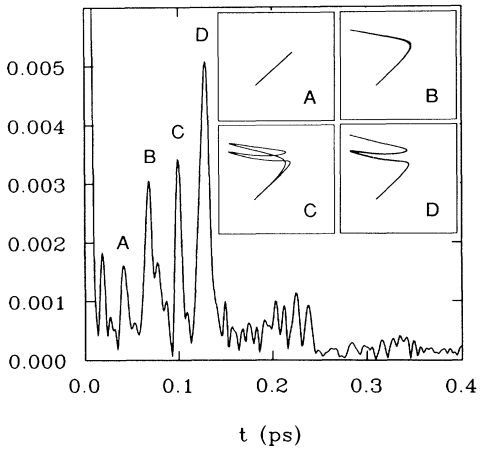

FIG. 2. Absolute value of autocorrelation function. The largest of the recurrences are close to the times of trajectories returning to the Franck-Condon region, shown in projection on the r_2-vs-r_1 plane.

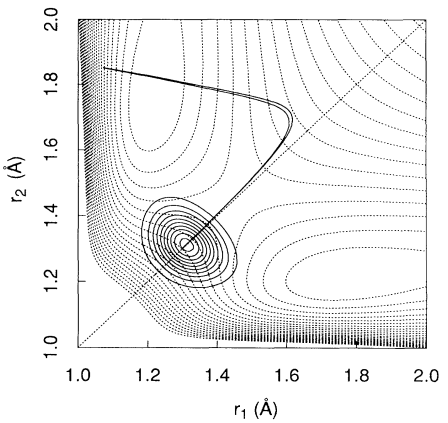

FIG. 3. Trajectory B of Fig. 2 in relation to the wave function $\psi_0(r_1,r_2,\theta)$ and the $^1B_2$ potential surface of Ref. 2, both taken at the ground-state equilibrium angle $\theta=116°$. Those configurations in which ψ_0 has significant amplitude can be regarded as the Franck-Condon region. The dashed line $r_1=r_2$ represents the molecular configurations of C_{2v} geometry.

ally from the accompanying $^1A_1$ surface[2] with C_{2v}-geometry minima, and is also shown in Fig. 3. The initial loss of overlap between $\Phi(r_1,r_2,\theta,0)$ and $\Phi(r_1,r_2,\theta,t)$ has been ascribed[19-22] to motion of the wave packet primarily down the $r_1=r_2$ C_{2v}-symmetry ridge toward the saddle point. (There is also some motion in θ, although this does not affect the symmetry.) The bulk of the wave packet bifurcates before a complete oscillation on this ridge and leaves directly out the two exit channels.

This leaves unexplained the succession of small features ($<0.5\%$) in the autocorrelation function at $t=19$, 41, 68, 99, and 128 fs. These features correspond directly to the fine structure discernible in Fig. 1. After the first plateau, a second plateau region of lower amplitude but similar duration occurs, followed by a third. The strong feature at 128 fs was anticipated in Ref. 20 on the basis of the roughly 250-cm^{-1} spacing discernible in $\epsilon(\omega)$ under intermediate (vibrational) resolution. The abundance of important earlier peaks was not as obvious, however. This indicates that small but non-negligible portions of the packet $\Phi(r_1,r_2,\theta,t)$ return to the general Franck-Condon region on a time scale typical of very low-frequency vibrational modes. If the precise significance of these early-to-intermediate events in the autocorrelation function can be identified, an explanation of the oscillations in the Hartley band will finally be available.

We proceeded in part as in recent works on the quasi-Landau problem[5-11] and on H_3^+.[12,13] A limited search was made for periodic classical trajectories on the Sheppard-Walker $^1B_2$ surface, integrating Hamilton's equations of motion using the classical triatomic kinetic energy (for $J=0$) in the bond coordinates r_1, r_2, and θ.[23] The first search was restricted to those trajectories starting from rest in C_{2v} geometry within the Franck-Condon region. The energy region of greatest interest here is at the maximum of the absorption spectrum, $\sim$7000 cm^{-1} above the energetic threshold for $O_2(^1\Delta_g)+O(^1D)$. As a result, the trajectories are quite chaotic, and C_{2v} symmetry can be destroyed by buildup of numerical roundoff error within 100–200 fs if care is not exercised.

The shortest periodic C_{2v} trajectory was found to be essentially a symmetric stretching in r_1 and r_2. An example of this orbit, projected into the r_1-r_2 plane, is shown in inset A of Fig. 2. The accompanying bending motion is not explicitly shown. This particular orbit has a period of 42.8 fs, corresponding closely to the feature in the autocorrelation function of 41 fs. The initial conditions leading to this periodic orbit can be continuously varied down to locations barely above the saddle point.[24] This orbit is also unstable to any asymmetry in the initial conditions, as expected and found by Berblinger, Pollak, and Schlier[12] in the similar case of H_3^+. The symmetric-stretch orbit, while unstable, is known to be capable of "scarring" the quantum-mechanical wave functions.[25]

Longer-period orbits in C_{2v} geometries were found, but either had periods >200 fs or fell far outside the Franck-Condon region. Further searching for new C_{2v} periodic trajectories (Lissajou figures) with the initial rest condition relaxed was unsuccessful. It was tentatively concluded that the C_{2v} orbits could not explain the majority of the features in the autocorrelation function.

A number of trajectories were then run with asymmetric initial conditions. Most such three-dimensional trajectories with energies near the absorption maximum lead to dissociation within a few hundred femtoseconds. Concessions needed to be made to limit the scope of our search for periodic orbits to a practical level. First, ini-

tial conditions were chosen only near the symmetry ridge, but still close to the center of the Franck-Condon region. Second, all trajectories were started at rest. Finally, it was decided to relax the condition of perfect periodicity, or closure, of the trajectories. Thus, initial values of r_1 and r_2 were chosen close to the ground-state minimum configuration and θ was varied until a trajectory returned to near the starting point within the Franck-Condon region.

The earliest nearly periodic trajectories found are insets B (70.2 fs) and C (103.1 fs) in Fig. 2. These match very well the prominent peaks in the correlation function at 68 and 99 fs, respectively. After this we start to find more and more examples of returning trajectories, with one at 131.2 fs (D in Fig. 2) actually periodic to two significant figures. Trajectories A–D exhibit a progression in which both bonds start lengthening together and r_2 undergoes one circuit while r_1 goes through successively one, two, three, and four circuits. The Hartley-band oscillations visible under intermediate resolution appear to be chiefly correlated with families of orbits like these which return to the Franck-Condon region.[26]

At this point, fine tuning the search is of limited value for several reasons: (1) An assignment has been obtained for all but the 19-fs feature, providing a consistent interpretation for most of the apparent progression in the first plateau region of the autocorrelation function. (2) While the details of the potential surface around the Franck-Condon region are probably reliable,[2,22] the trajectories shown in Fig. 2 move around the global minima, about which we are less certain. (3) One expects that periodic orbits not only exist, but fall on continuous or dense manifolds in phase space, making their mapping an immense task. (4) It is likely that perfect periodicity of a trajectory is not essential in the underlying classical-quantal correspondence for these rather early features. Evidence of this effect has been obtained by Du and Delos[8] in the case of the quasi-Landau oscillations in hydrogen. These considerations lead much too far afield for present purposes. They will, however, be important in any attempt (e.g., as in Ref. 8) to calculate the autocorrelation function on the basis of classical trajectories.

Two phenomena remain unexplained. The very early feature at 19 fs is not part of the progression based on the Sheppard-Walker surface. It is, in fact, even faster than the ~22-fs vibrational period of $O_2(^1\Delta g)$,[27] the adiabatic product of the dissociation. This feature seems to arise from oscillations localized around the maximum of the absorption cross section.[24] The oscillations are presumably not due to photolysis products, however, since neither $O_2(^1\Delta_g)$ nor $O_2(^3\Sigma_g^-)$ (accessible by nonadiabatic interactions) exhibit continuous absorption in this energy region. Hot-band activity could in principle contribute to early features in the autocorrelation function (primarily through the low-frequency bending mode at $T=195$ K).

The other unexplained phenomenon is the sudden dropoff in the autocorrelation function after the intense 128-fs feature. Inhomogeneous broadening of the spectrum due to the rotational distribution of the initial sample certainly contributes a gradual decay[17,28] over the course of the 400 fs shown in Fig. 2, but is unlikely to cause sudden decay. Another possibility considered was pseudorotation, or motion between the symmetrically related minima on the $^1B_2$ surface, suggested by findings in Ref. 2 that 9.4% of the trajectories were complex enough to end in central atom dissociation. There is still room for pseudorotation effects to contribute to the absorption oscillations, but our results say nothing about this. Tannor has been independently pursuing this possibility.[29] With the present evidence that the time progression corresponds to a series of distinct trajectories, relative stability of the orbits will also become an important question. The effect on the autocorrelation function is expected to be greatest for the most stable orbits (but still the unstable symmetric-stretch trajectory can contribute a characteristic peak[25]).

It has been shown that specific types of trajectories starting from and returning to the Franck-Condon region of ozone correspond very closely with intermediate-time features in the autocorrelation function, that is, with spectral oscillations at a vibrational level of resolution. These small features indicate that portions of the quantum-mechanical wave function "reassemble" in or near the original molecular configuration. A more extended examination of the classical dynamics of O_3 is therefore warranted in the future. This will be especially worthwhile if newer and more extensive *ab initio* calculations are performed for the potential surfaces, and if a direct uv absorption spectrum is taken of jet-cooled O_3 to alleviate the rotational congestion.

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