Reprinted from The Journal of Physical Chemistry, 1982, *86*, 2113.

Semiclassical Theory of Intensities of Vibrational Fundamentals, Overtones, and Combination Bands

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Semiclassical Theory of Intensities of Vibrational Fundamentals, Overtones, and Combination Bands

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(Received: September 2, 1981)

Quantum mechanical and semiclassical results are compared for the spectrum of the Morse oscillator. When an average quantum number $[(n + m)/2]$ trajectory is employed for an $n \rightarrow m$ transition, good agreement is obtained between the quantum and semiclassical intensities and between the frequencies, for the fundamental and the overtones studied. Spectra of nonrotating OCS in the quasiperiodic and chaotic regions are presented, and the intensities of a number of overtones and combination bands are calculated. Even very low intensity transitions are observed.

I. Introduction

There has been considerable interest in recent years in the semiclassical analysis of coupled anharmonic systems.[1,2] These studies have been motivated in part by the difficulty of exact quantum mechanical calculations on systems as small as bent triatomics when one attempts to include rotations and all of the vibrational–rotational couplings. Indeed, there appear to be no exact calculations on triatomics for other than $J = 0$. Because of this difficulty, many workers[1,2] have investigated various bound state semiclassical methods, exact and approximate, using the Bohr–Sommerfeld–Einstein–Keller quantum condition

$$\oint_{C_i} \sum \mathbf{p}\cdot d\mathbf{q} = (n_i + \delta_i)h (i = 1, ..., M) \qquad (I.1)$$

Here, $\mathbf{p}$ and $\mathbf{q}$ are $2M$ conjugate momenta and coordinates, n_i is a quantum number, the C_i are M topologically independent paths, and the δ_i are known constants. A number of small systems have been investigated with these techniques, and the results have, in general, been encouraging. In the quasiperiodic regime the classical trajectory uniformly covers an M-dimensional surface (a torus) in $2M$-dimensional phase space. The motion is characterized by the M constants of the motion (left-hand side of eq I.1) and by the M initial phases canonically conjugate to these M actions.

Recently, we obtained from a classical trajectory the power spectrum of any classical mechanical variable.[3-5] It was shown[3] that the spacings of the quantum mechanical vibrational eigenvalues agree well with those deduced from the classical vibration frequencies, in the classically quasiperiodic regime. It was also shown that in the classically chaotic regime a line spectrum was obtained while in the chaotic regime the spectrum was "dispersed".[3] This method of generating a molecular spectrum from classical trajectories has now been applied by several investigators, e.g., ref 6–11.

We used a zeroth-order Hamiltonian to define semiclassically the initial conditions (the "eigentorus") for the trajectory used to obtain the classical autocorrelation function. The Fourier transform of this correlation function then provided the power spectrum.[3] Later, we also showed for one spectrum that good agreement with quantum mechanical results for the spectral intensity could also be obtained.[5]

In the next section of this paper the basic semiclassical formulae are presented for the spectra. In section III the quantum mechanical expression for the intensity is given for the Morse oscillator. In section IV the semiclassical method is tested by comparing it with the quantum analytic results in section V for the fundamental and various overtones. In section VI the spectrum of a nonrotating OCS molecule is obtained with this semiclassical spectral method, and the intensities of some fundamentals and a number of overtones and combination bands are calculated.

II. Semiclassical Correspondence

In deducing the spectrum from a classical trajectory we first calculate[3] the classical autocorrelation function by averaging the quantity of interest, such as the dipole moment $\mu(t)$, over the appropriate ensemble. The reduced

† Contribution no. 6518.

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(2) I. C. Percival, *Adv. Chem. Phys.*, 36, 1 (1977), and references cited therein.
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(4) D. W. Noid, M. L. Koszykowski, M. Tabor, and R. A. Marcus, *J. Chem. Phys.*, 72, 6169 (1980).
(5) D. W. Noid, M. L. Koszykowski, and R. A. Marcus in "Classical Semiclassical and Quantum Mechanical Problems in Mathematics, Chemistry and Physics", K. Gustavson and W. P. Reinhardt, Ed., Plenum Press, New York, 1981, p 181.
(6) J. D. McDonald and R. A. Marcus, *J. Chem. Phys.* 65, 2180 (1976).
(7) K. D. Hansel, *Chem. Phys.*, 33, 35 (1978).
(8) G. E. Powell and I. C. Percival, *J. Phys. A*, 12, 2053 (1979).
(9) D. Poppe, *Chem. Phys.*, 45, 371 (1980).
(10) S. C. Farantos and J. N. Murrell, *Chem. Phys.*, 55, 205 (1981).
(11) An interesting analysis of rotation and vibration of diatomic molecules in condensed phases using classical trajectories to calculate the spectrum has been made by P. H. Berens and K. R. Wilson, *J. Chem. Phys.*, 74, 4872 (1981); P. H. Berens, S. R. White, and K. R. Wilson, *ibid.*, 75, 515 (1981).

classical spectral intensity[12] I is then given by the Fourier transform of the autocorrelation function:

$$I = \frac{1}{2\pi}\int_{-\infty}^{\infty}\langle\mu(0)\cdot\mu(t)\rangle e^{i\omega t}\,dt \qquad \text{(II.1)}$$

In the quasiperiodic regime the ensemble needed to obtain the spectral frequencies consists of an ensemble of trajectories, but we showed[3] that a single trajectory can suffice when an equivalent formula, given later, is used.

The justification for using classical trajectories to obtain semiclassical spectra is as follows:

Equation II.1 can be rewritten as [12]

$$I = \sum_m |\langle m|\mu|n\rangle|^2\delta(\omega - \omega_{mn}) \qquad \text{(II.2)}$$

where we have considered the case where only state $|n\rangle$ is initially populated and where ω_{mn} is the transition frequency

$$\omega_{mn} = \frac{1}{\hbar}(E_m - E_n) \qquad \text{(III.3)}$$

We shall use the semiclassical wave function

$$\langle w|n\rangle = e^{2\pi i n w} \qquad \text{(II.4)}$$

where w is the angle variable (e.g., ref 13). The matrix element for the dipole operator becomes, on introducing the identity operator $\int_0^1|w\rangle\,dw\,\langle w|$

$$\begin{aligned}\langle m|\mu|n\rangle &= \int_0^1\langle m|w\rangle\langle w|\mu|n\rangle\,dw \\ &= \int_0^1\langle m|w\rangle\mu(\mathbf{J},\mathbf{w})\langle w|n\rangle\,dw \\ &= \int_0^1 e^{-2\pi i m w}\mu(\mathbf{J},\mathbf{w})e^{2\pi i n w}\,dw \qquad \text{(II.5)}\end{aligned}$$

where the semiclassical action operator $\mathbf{J}$ is $[\hbar/i)\,\partial/\partial w + {}^1/_2\hbar]$ for an oscillator.[14] Performing the operation gives

$$\langle m|\mu|n\rangle = \int_0^1\mu(J_n,w)e^{2\pi i(n-m)w}\,dw \qquad \text{(II.6a)}$$

and similarly

$$\langle n|\mu|m\rangle = \int_0^1\mu(J_m,w)e^{2\pi i(m-n)w}\,dw \qquad \text{(II.6b)}$$

where J_n is the classical action for the torus corresponding to the semiclassical state n. For an oscillator one has

$$J_n = (n + {}^1/_2)h \qquad \text{(II.7)}$$

We have written the above equations in terms of only one coordinate for notational simplicity. The extension to M coordinates is clear, e.g., dw becomes $\prod_i dw_i$, nw becomes $\sum_i n_i w_i$, etc.

Equation II.6 should satisfy the condition that $\langle m|\mu|n\rangle$ be Hermitean, but does so only approximately; the semiclassical analysis leading to (II.6) assumes that $|n - m| << n$. To satisfy the Hermitean property we replace J_n and J_m in eq II.6 by their mean value, $(J_n + J_m)/2$:

$$\langle m|\mu|n\rangle = \int_0^1\mu\left(\frac{J_n + J_m}{2},w\right)e^{2\pi i(n-m)w}\,dw \qquad \text{(II.8)}$$

This expression is then introduced into eq II.2 to obtain the intensity.

One sees from (II.8) that the matrix element appearing in eq II.2 is the n–mth Fourier coefficient for the dipole operator, evaluated at an action variable $(J_n + J_m)/2$. Similarly, the frequency ω_{mn} is replaced by the classical frequency for a system with the action variable $(J_n + J_m)/2$, rather than J_n or J_m alone.

Equations II.2 and II.8 are the equations previously used[3] (eq 2.7 and 2.9 there), although ω_{mn} was, instead, replaced by $[\omega(J_m) + \omega(J_n)]/2$, an approximation less accurate than the present one (see below).

For a system in a particular quantum state the corresponding semiclassical autocorrelation function is an average over appropriate angle values (initial vibrational and rotational phases). It was shown (cf eq 2.10 of ref 3) to be equal to

$$I = \frac{1}{2\pi}\lim_{T\to\infty}\left\langle\frac{1}{T}\left|\int_0^T\mu(t)\exp(-i\omega t)\,dt\right|^2\right\rangle \qquad \text{(II.9)}$$

It was noted in ref 3 that, for a nondegenerate system in a given quantum state, a single trajectory suffices for use in (II.9), and so for that case the $\langle\ \rangle$ sign can be ignored. In contrast, eq II.1 for the intensity requires an ensemble of trajectories, a sample over initial phases (the initial angle variables). In a degenerate system the $\langle\ \rangle$ sign in (II.9) denotes an average over angle variables canonically conjugate to certain action variables, namely, those absent in the Hamiltonian.

III. Quantum Mechanical Spectral Lines

The well-known Morse oscillator Hamiltonian[14] is given by

$$H = \frac{p^2}{2\mu} + D(1 - e^{-a(r-r_e)})^2 \qquad \text{(III.1)}$$

The wave functions resulting from the solution to the Schrödinger equation for this Hamiltonian are[14]

$$\psi_n(x) = N_n e^{-z/2}z^{b/2}L_n^b(z) \qquad \text{(III.2)}$$

where

$$N_n = \left[\frac{abn!}{\Gamma(k-n)}\right]^{1/2}\cdot \qquad z = ke^{-a(r-r_e)} \qquad \text{(III.3)}$$

$$b = k - 2n - 1$$

$$k = 1/\chi_e = 2\mu\omega_e/\hbar a^2 \qquad \omega_e = a(2D/\mu)^{1/2} \qquad \text{(III.4)}$$

with ω_e being the angular frequency and $\omega_e\chi_e$ the anharmonicity constant, defined by eq III.4. We shall denote by b' the expression

$$b' = k - 2m - 1 \qquad \text{(III.5)}$$

For the present purpose of comparison of classical and quantum results we shall write μ as a constant plus $r - r_e$. Thereby, with $m \neq n$

$$\mu_{mn} = \langle m|\mu|n\rangle \equiv \langle m|(r - r_e)|n\rangle \qquad \text{(III.6)}$$

Equations III.2–III.5 yield

$$\mu_{mn} = \frac{N_m N_n}{a}\int_0^{ke^{as_e}} e^{-z}z^{(b/2+b'/2-1)}a^{-1}\ln(k/z)L_m^{b'}(z)L_n^b(z)\,dz \qquad \text{(III.7)}$$

where we have changed the variable of integration from r to z.

By extending the upper limit to infinity, a negligible error is introduced into the integration and one obtains, noting that ψ_n and ψ_m are orthogonal

$$\mu_{mn} = -\frac{N_m N_n}{a}\int_0^{\infty} e^{-z}z^{(b/2+b'/2-1)}a^{-1}\ln z L_m^{b'}(z)L_n^b(z)\,dz \qquad \text{(III.8)}$$

The Laguerre polynomials are introduced, and after

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(14) P. M. Morse, *Phys. Rev.*, 34, 57 (1929).

evaluation of the integral[15] and use of the identity[16] for $m > n$

$$\frac{n!}{m!}\frac{\Gamma(k-n)}{\Gamma(k-m)}\sum_{i=0}^{n}\frac{(m+i-n-1)!\Gamma(k+i-m-n-1)}{i!\Gamma(k+i-2n)} = \frac{1}{(m-n)(k-m-n-1)} \quad \text{(III.9)}$$

one obtains[15]

$$\mu_{mn} = \frac{(-1)^{m-n+1}}{a(m-n)(k-m-n-1)}\left(\frac{m!}{n!}\frac{\Gamma(k-m)}{\Gamma(k-n)}bb'\right)^{1/2} \quad (m > n) \quad \text{(III.10)}$$

This quantum mechanical expression is then introduced into eq II.2.

The problem of calculating matrix elements for the Morse oscillator was treated by Dunham[17] for specific transitions, by others,[18] and recently by Gallas,[15] who obtained expressions for matrix elements of all powers of the displacement coordinate.

IV. Semiclassical Spectral Lines

In this section we compare the frequencies of the quantum mechanical and the semiclassical spectral lines first. Comparison of eq IV.1 and IV.3 shows that the semiclassical (WKB) expression for the eigenvalues for a Morse oscillator agrees exactly with the quantum mechanical expression when (I.1) is introduced. However, what we are concerned with in this paper is how the frequency obtained from a single classical trajectory agrees with the quantum mechanical fundamental frequencies ($n \rightarrow n+1$) and overtones ($n \rightarrow m$, $m > n+1$). What interpolation or rule will provide good or even exact agreement for the Morse oscillator?

The quantum mechanical energy levels of a Morse oscillator are given by[14]

$$E_n = (n+\tfrac{1}{2})\hbar\omega_e - (n+\tfrac{1}{2})^2\hbar\omega_e\chi_e \quad \text{(IV.1)}$$

The angular frequency ω_{mn} is $(E_m - E_n)/\hbar$ and so is

$$\omega_{mn} = (m-n)\omega_e - (m-n)(n+m+1)\omega_e\chi_e \quad \text{(IV.2)}$$

The classical energy as a function of the action J is [19]

$$E = (J\omega_e/2\pi) + J^2\omega_e\chi_e/2\pi h \quad \text{(IV.3)}$$

(The χ_e has an h which cancels the h in the denominator.) The classical angular frequency $\omega(J)$ is $2\pi\nu(J)$, where ν is $\partial E/\partial J$. Thereby

$$\omega(J) = \omega_e + 2J\omega_e\chi_e/h \quad \text{(IV.4)}$$

and so classically the lth overtone is

$$l\omega(J) = l\omega_e + 2Jl\omega_e\chi_e/h \quad \text{(IV.5)}$$

If we replace J by its mean value for the $n \rightarrow m$ transition, $(J_n + J_m)/2$, we obtain

$$l\omega(J) = l\omega_e + (n+m+1)l\omega_e\chi_e \quad \text{(IV.6)}$$

This expression is seen to be identical with the quantum mechanical one, eq IV.2, remembering that $m - n = l$. To obtain this exact agreement for the Morse oscillator it is seen to be essential that the classical frequency $\omega(J)$ be evaluated at J equal to $(J_n + J_m)/2$. To obtain the overtone corresponding to $E_m - E_n$ for this and other systems we shall use in the following the Fourier transform of the correlation function obtained from the classical trajectory whose action is $(J_n + J_m)/2$.

We turn next to the semiclassical intensities. The vibrational coordinate for a Morse oscillator can be written as[20]

$$(r - r_e) = (1/a)\ln\{[1 - P\cos(\omega_v t + \phi)]/(1 - P^2)\} \quad \text{(IV.7)}$$

where ϕ is an arbitrary phase angle and ω_v is given by

$$\omega_v = \omega_e(1 - P^2)^{1/2} \quad \text{(IV.8)}$$

P is related to the vibrational energy E by[20]

$$P = (E/D)^{1/2} \quad \text{(IV.9)}$$

and so is related to J by (IV.3). Calculation shows that the ω_v defined by (IV.8) is the angular frequency, $2\pi(\partial H/\partial J)$, at the given J.

The dipole moment, taken as $r - r_e$ for the present comparison and so given by (IV.7), can be expanded in the Fourier series

$$r - r_e = a_0/2 + \sum_{l=1}^{\infty} a_l \cos l(\omega t + \phi) = \tfrac{1}{2}\sum_{l=-\infty}^{\infty} a_l e^{il(\omega t+\varphi)} \quad \text{(IV.10)}$$

where $a_l = a_{-l}$. It has been shown that the a_l are given by[20,21]

$$a_l = \frac{2(-1)^l}{la}\left(\frac{1-(1-P^2)^{1/2}}{P}\right)^l \quad (l > 0) \quad \text{(IV.11)}$$

In applying (IV.11) to calculate the intensity of a transition $n \rightarrow m$ using (II.2), with P related to J via (IV.3) and (IV.9), we shall set $J = (J_n + J_m)/2$. I.e., we have

$$J = \left(\frac{n+m}{2} + \tfrac{1}{2}\right)h \quad \text{(IV.12)}$$

The l in (IV.10)–(IV.11) is simply m–n, as one sees by comparing (II.8) and (IV.10) and noting that $2\pi w$ equals $\omega t + \phi$. Accordingly, the semiclassical matrix element μ_{mn}^{sc} is given by

$$\mu_{mn}^{sc} = \tfrac{1}{2}a_l \quad \text{with} \quad l = m - n \quad (m > n) \quad \text{(IV.13)}$$

Classical rotational corrections to the a_l expressions have been given by Tipping.[21a]

Before proceeding with the numerical results, it is useful to compare eq III.10 and IV.11 analytically. In (III.10), $k - m - n - 1$ is the arithmetic mean of b and b' and so, in the first approximation, can be replaced by its geometric mean (thereby neglecting terms second order in $(m - n)$). The $m!$ contains $m - n$ factors more than does $n!$, and the arithmetic average of these terms is $(m + n + 1)/2$. Replacing the geometric average by the arithmetic average, $m!/n!$ equals approximately $[(m + n + 1)/2]^{m-n}$. The $\Gamma(k - n)$ contains $m - n$ more factors than $\Gamma(k - m)$ and their arithmetic average is $k - \frac{1}{2}(m + n + 1)$. Again replacing the $m - n$ factors by their geometric average to the m–nth power, we now have

$$\mu_{mn} \simeq -\left(\frac{N}{N-k}\right)^{m-n}\frac{1}{a(m-n)} \quad \text{(IV.14)}$$

where

$$N = \tfrac{1}{2}(n + m + 1) \quad \text{(IV.15)}$$

(15) J. A. C. Gallas, *Phys. Rev., A*, 21, 1829 (1980).
(16) E. R. Hanson, "A Table of Series and Products", Prentice-Hall, Englewood Cliffs, NJ, 1975.
(17) J. L. Dunham, *Phys. Rev.*, 35, 1347 (1930).
(18) E.g., H. S. Heaps and G. Herzberg, *Z. Phys.*, 133, 48 (1952), and other references cited therein and in ref 15.
(19) C. C. Rankin and W. H. Miller, *J. Chem. Phys.*, 55, 3150 (1971).
(20) I. E. Sazonov and N. I. Zhirnov, *Opt. Spectrosc.*, 34, 254 (1973).
(21) (a) R. H. Tipping, *J. Mol. Spectrosc.*, 53, 402 (1974). (b) One integrates the Fourier expression for a_l by parts, uses a cosine addition formula, and then uses eq 1 in Section 3.613 of I. S. Gradshteyn and I. M. Ryzhik, "Table of Integrals, Series and Products", Academic Press, New York, 1965, p 366.

TABLE I: Comparison of Quantum Mechanical and Semiclassical Spectral "Intensities" ($|\mu_{mn}|^2$) for the Morse Oscillator for HF[a,b]

transition $m \rightarrow n$	quantum[c] int	$I[(n+m]/2)^d$	$I(n)^e$	$(I(n)+I(m))/2^f$
$0 \rightarrow 1$	5.4×10^{-2}	5.4×10^{-2}	3.0×10^{-2}	4.7×10^{-2}
$0 \rightarrow 2$	6.1×10^{-4}	6.1×10^{-4}	7.2×10^{-5}	6.9×10^{-4}
$0 \rightarrow 3$	1.7×10^{-5}	2.6×10^{-5}	3.3×10^{-7}	5.3×10^{-5}
$0 \rightarrow 4$	8.6×10^{-7}	15×10^{-7}	2.2×10^{-9}	8.6×10^{-6}

[a] The "intensities", denoted by I in the columns for notational brevity, are really $|\mu_{mn}|^2$ or $|a_l/2|^2$ and are in units of A^2. They are also the same as "integrated band intensities", as one sees by integrating a δ function in (II. 2) over a small ω-interval centered about $\omega = \omega_{mn}$. [b] For purposes of this comparison the dipole moment is written as $r - r_e$ plus a constant. [c] Equation III. 10. [d] Semiclassical. Equations IV. 11 and IV. 12. [e] Unsymmetrized semiclassical. [f] "Average semiclassical".

The classical expression can be simplified by recognizing, after some manipulation, that

$$1 - (1 - P^2)^{1/2} = Ja/(8\pi^2\mu D)^{1/2} \qquad \text{(IV.16)}$$

$$P^2 = \frac{2Ja}{(8\pi^2\mu D)^{1/2}} - \frac{J^2a^2}{8\pi^2\mu D} \qquad \text{(IV.17)}$$

and, thereby, on using (III.4) and (IV.12)

$$\frac{a_l}{2} = \left(\frac{N}{N-k}\right)^l \frac{1}{al} \qquad \text{(IV.18)}$$

which is identical with the quantum mechanical result (IV.14). The approximation made in (IV.14) was in the replacement of geometric averages by arithmetic ones. When one considers that the approximation made in (II.8) involves using an arithmetic mean of J's, instead of using, via ladder operator in the μ of (II.5), a more geometric method of calculating $n \rightarrow m$ transitions, this arithmetic mean - geometric mean relationship between (III.10) and IV.11) is not surprising.

V. Comparison of Quantum Mechanical and Semiclassical Spectra

(a) *Comparison of Quantum Mechanical and Semiclassical Spectra.* We have chosen to apply the method to HF using[22] $D = 5.716$ eV, $r_e = 1.75$ a_0, and $a = 1.22$ a_0^{-1}, where a_0 is the Bohr radius. The results are shown in Table I. Also shown for comparison are some semiclassical results one would have obtained had some approximation other than $J = (J_n + J_m)/2$ been used in eq II.8 for the semiclassical matrix element μ_{mn}.

(b) *Fundamentals and Overtones of OCS.* In this section we use the method of ref 3 to obtain from classical trajectories the spectrum of OCS. The anharmonic force field and the dipole moment function given for OCS in ref 23 and 24a, respectively, were employed. The Hamiltonian used is given by eq 29–31b of ref 25 for a nonrotating molecule. The dipole moment function taken from ref 24a was devised there by fitting the calculated $|\mu_{mn}|^2$'s to experimental integrated band intensities (using equations in ref 24b), employing a potential different from the present one. Thus, the $|\mu_{mn}|^2$ given later in Table II need not agree with those in ref 24a nor, thereby, with the data.

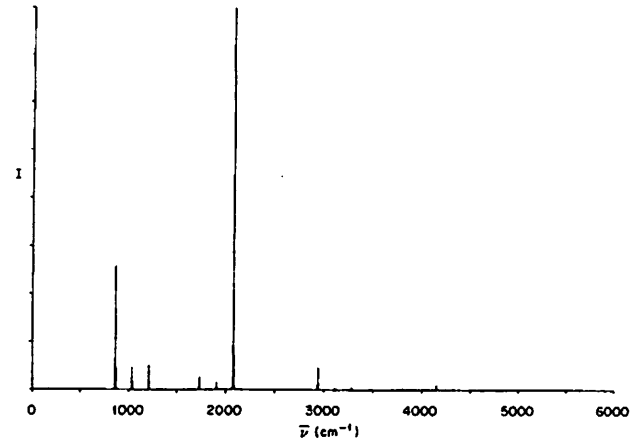

Figure 1. Vibrational spectrum of OCS in the classically quasiperiodic regime, in state (0,0°,0). Noticeable peaks are for ν_1, $2\nu_2$, $\nu_3 - \nu_1$, $2\nu_1$, $\nu_1 + 2\nu_2$, ν_3, and $\nu_1 + \nu_3$ at 865.2, 1037.8, 1210.3, 1730.4, 1903.0, 2075.5, and 2940.7 cm^{-1}, respectively. The $4\nu_2$ peak at 2075.6 cm^{-1} is in Fermi resonance with ν_3 and is hidden. The $4\nu_2$ and ν_3 peaks are resolved in the spectrum for the "(0,0°,$^1/_2$)" state, occurring there at 2075.5 and 2084.0 cm^{-1}, respectively. The $4\nu_2$ peak is one order of magnitude less in intensity than the $2\nu_2$ peak.

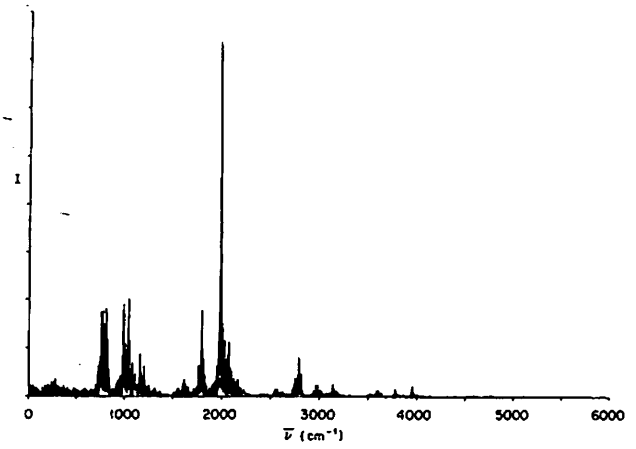

Figure 2. Vibrational spectrum of OCS in the classically chaotic regime, at an energy corresponding to the state (3,4°,2).

The initial conditions were chosen semiclassically by using the zeroth-order Hamiltonian (and the initial coordinates were $q_1 = q_2 = q_3 = 0$). Hamilton's equations were solved by using a standard program[26] for solving coupled differential equations. The $\mu(t)$ was calculated from the trajectory. (The numbers of t values used are given later in footnotes b and c of Table II.) A Fourier transfrom of the $\mu(t)$ was next computed (NAG program C06AAA) by using a CRAY 1S. In Figures 1 and 2 power spectra for the sum of coordinates $q_1 + q_2 + q_3$ are plotted for the (0,0°,0) quantum state (energy of 1745.9 cm^{-1}) and for an energy corresponding to the (3,4°,2) quantum state (energy of 10 652.4 cm^{-1}), respectively. The former is in the classically quasiperiodic regime and the latter is in the classically chaotic regime. In the chaotic case the correlation function associated with a single trajectory decays exponentially with superimposed oscillations while in the

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(24) (a) A. Foord and D. H. Whiffen, *Mol. Phys.*, 26, 959 (1973). Due to the differences in the scaling of coordinates in ref 24a and 25, the constants taken from the former were rescaled for present purposes. (b) J. Overend in "Infrared Spectroscopy and Molecular Structure", M. Davies, Ed., Elsevier, New York, 1963, p 345.

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(26) M. K. Gordon, Sandia Laboratories Report, SAND75-0211. For a discussion of the algorithm, see L. F. Shampine, and M. K. Gordon "Computer Solution of Ordinary Differential Equations", Freeman, San Francisco, 1975.

TABLE II: Relative "Intensities" ($|\mu_{mn}|^2$) of Overtones of OCS[a]

transition ν, $n \rightarrow m$		$I([n+m]/2)$[b]	$I(n)$[c]	$\bar{\nu}$, cm^{-1} present[b]	quantum[d]	harmonic
ν_1	$0 \rightarrow 1$	1.00[a]	1.00[a]	861.4	859.0	875.6
	$0 \rightarrow 2$	9.4×10^{-2}	7.4×10^{-3}	1715.4	1710.6	1751.2
	$0 \rightarrow 3$	2.0×10^{-3}	2.7×10^{-5}	2561.4	2555.1	2626.8
	$0 \rightarrow 4$	1.1×10^{-4}	1.2×10^{-7}	3400.2	3395.2	3502.4
	$0 \rightarrow 5$	3.1×10^{-6}		4231.6		4378.0
ν_3	$0 \rightarrow 1$	1.00[a]	1.00[a]	2064.0	2062.0	2092.5
	$0 \rightarrow 2$	5.7×10^{-4}	1.8×10^{-4}	4104.7	4104.4	4185.0
	$0 \rightarrow 3$	2.8×10^{-6}	1.2×10^{-7}	6126.5		6277.5
	$0 \rightarrow 4$	7.6×10^{-8}		8124.6		8370.0
$\nu_1 + \nu_3$	$0 \rightarrow 1$[e]	1.00[a]	1.00[a]	2922.6	2918.1	2968.1
	$0 \rightarrow 2$[e]	2.3×10^{-4}	4.7×10^{-6}	5769.9		5936.2

[a] These "intensities" are really the $|\mu_{mn}|^2$'s (cf. footnote *a* of Table I) relative to the relevant $0 \rightarrow 1$ transition. The $|\mu_{mn}|^2$'s for the $0 \rightarrow 1$ ν_1 and the $0 \rightarrow 1$ $\nu_1 + \nu_3$ bands are 0.034 times and 0.010 times of $0 \rightarrow 1$ ν_3 band, respectively. The absolute value of $|\mu_{mn}|^2$ for the $0 \rightarrow 1$ ν_1 band is 4.0×10^{-3} D^2. ν_1 is the symmetric stretch, ν_3 is the asymmetric stretch, and the bend is ν_2. The bend does not contribute much to the particular dipole spectral function studied. All transitions indicated are those at zero vibrational angular momentum. [b] Semiclassical. 32,768 points for $\mu(t)$, taken from an effectively continuous trajectory (absolute accuracy in integration routine of 10^{-7}), sufficed to yield sufficient intensity for all transitions in this column. The $\bar{\nu}$'s and I's are for the $(n+m)/2$ trajectories. [c] Unsymmetrical semiclassical. [d] Reference 23. [e] I.e., (0,0°,0) → (1,0°,1) and (0,0°,0) → (2,0°,2), respectively.

quasiperiodic case there are only oscillations.[27] The spacing between the frequency points used to calculate these spectra was, to two significant figures, 0.38 cm^{-1}, and so the precision of the lines in the spectrum is approximately ±0.4 cm^{-1}. The quasiperiodic and chaotic trajectories in Table II had integration times of about 25 ps and could be back-integrated to seven places and to five places, respectively.

In Table II the intensities of the overtones are given relative to the relevant fundamental. The intensities of some combination bands are also given. The sensitivity of the results to different numbers of points (twice as many or half as many) and to different spacings between the spectral points (half as large or twice as large) was tested. The results for any given frequency varied only about 20–30%, with change of number of points or their spacings, when the amplitude exceeded the background by at least 10:1. The frequencies and the quantum mechanically calculated frequencies[23] are also given.

In these spectra, the height of a peak is proportional to the time of a trajectory, and to calculate the absolute intensity one divides by the trajectory time (cf. eq II.9). The result is then independent of the trajectory time. Longer trajectories reduce the width at the base of the line[3] but do not alter the ratio of height of $|\int_0^T \mu(t) \exp(-i\omega t)\, dt|^2$ divided by trajectory time T.

It is useful to compare the $|\mu_{mn}|^2$ in Table II with those inferred[24a] from experimental integrated band intensities. The absolute value of $|\mu_{mn}|^2$ for the $0 \rightarrow 1$ ν_1 transition calculated here is 4.0×10^{-3} D^2, and experimentally[24a] is 4.6×10^{-3} D^2. The $|\mu_{mn}|^2$'s of $0 \rightarrow 1$ ν_1 and $\nu_1 + \nu_3$ bands are 0.034 and 0.010 times that of the $0 \rightarrow 1$ ν_3 band (footnote *a* of Table II) as compared with the experimental value[24a] of 0.039 and 0.011, respectively. The values of the $0 \rightarrow 2$ ν_1 and $0 \rightarrow 2$ ν_3 bands, given by 0.094 and 0.00057 in Table II are, experimentally, 0.092 and 0.0039. Agreement of the $|\mu_{mn}|^2$s can be improved by using a newly fitted dipole moment function. In separage calculations we have found that the theoretical $|\mu_{mn}|^2$'s are, particularly for the overtones, quite sensitive to the assumed dipole moment function and to the assumed anharmonic potential.

The calculation of the intensities of these overtones quantum mechanically is a straightforward problem in the one-dimensional case but becomes difficult in the several dimensional case, if a variational calculation is used: a large basis set is needed and high accuracy is required of the wave function for computing the matrix elements. Either approximate quantum calculations or a semiclassical method such as the present one may offer a suitable alternative.

Some useful aspects of the present method include its ease of calculation—the extremely simple programming and execution, no requirement of analytical evaluation of matrix elements for rapid calculation, no breakdown when Fermi resonance occurs, and ready applicability to larger systems. (Indeed, it has been so applied.[6,9]) The trajectory time used in the present results suffices for frequencies in the same range for larger molecules. Longer trajectory times are needed if the frequencies are smaller. The small deviations of the frequencies in Table II from the quantum mechanical ones appear to be due to the approximation inherent in using a single trajectory (an $^1/_2(n+m)$ trajectory) instead of using the energy difference of the n and the m eigentrajectories.

The present method applies regardless of whether the trajector is quasiperiodic or chaotic and, indeed, is one tool for distinguishing the two.[1] Its quantum implications are at present clear only in the quasiperiodic case, although it can presumably be used ot obtain *averaged* quantum results at high energies. Thus, a limitation of the method for predicting an *individual* spectral line $n \rightarrow m$ and its intensity is the restriction to conditions where the "state" $^1/_2(n+m)$ is classically quasiperiodic.

Previously, semiclassical calculations on OCS have been made for its eigenvalues,[25,28] though not for the intensities; a perturbative-iterative method was used. Good agreement was found for the eigenvalues for which the method converged. Another trajectory method for describing spectra has been given by Heller et al.[29] This method is complimentary to the present one in that it is more appropriate for electronic spectra (Franck–Condon) factors rather than for pure vibrational–rotational spectra.[1]

Acknowledgment. The research was supported by the U.S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corp. (at Oak Ridge), the National Science Foundation (at California Institute of Technology), and the DOE (at Sandia National Laboratories).

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