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Semiclassical Dressed State Theory for the Vibrational Excitation of a Morse Oscillator by Radiation

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A uniform semiclassical theory is developed to treat the interaction of a Morse oscillator with a monochromatic radiation field. The correspondence with quantum-mechanical dressed state theory for the Rabi and resonant excitation frequencies is demonstrated, and the semiclassical theory is used to describe resonant one- and two-photon absorption processes. The results are extended to state-to-state vibrational excitation in a polyatomic species.

Introduction

In the present paper, uniform semiclassical expressions are obtained for the resonant and Rabi frequencies for one- and two-photon absorption by a Morse oscillator. The correspondence of the results for these frequencies with quantum-mechanical dressed state theory¹ is described. This semiclassical treatment is derived for a diatomic molecule and is then adapted to the excitation of an isolated vibrational state in a polyatomic molecule. Experimental or theoretical studies of CH_3F ,² O_3 ,³ BCl_3 ,⁴ and SO_2 ,⁵ and of certain local mode molecules such as HDO ^{6a} and CHD_3 ,^{6b} suggest that such state-to-state behavior can be observed at low energies in some polyatomic molecules.

Many studies in the past few years^{7,8} have been devoted to the development of exact and approximate quantum-mechanical treatments for the vibrational excitation of a single anharmonic oscillator by an electromagnetic radiation field.⁹ In addition, there have been several classical and quantum resonance studies of

TABLE I: Quantum $\langle n_m+1|r|n_m \rangle$ vs. Semiclassical $\bar{r}(\bar{I}_m)$

n_m	$\langle n_m+1 r n_m \rangle$, au	$\bar{r}(\bar{I}_m)$, au
0	0.1246	0.1246
1	0.1781	0.1781
2	0.2205	0.2205
3	0.2575	0.2576
4	0.2912	0.2913
5	0.3228	0.3229

related driven oscillator systems,^{8,10-17} including the early work by Chirikov,¹⁵ Shuryak,¹⁶ and Zaslavsky.¹⁷ Recently, Gray¹⁸

(1) E.g., C. Cohen-Tannoudji in "Frontiers in Laser Spectroscopy", North-Holland Publishing Co., Amsterdam, 1977, p 14.

(2) W. K. Bischel, P. J. Kelly, and C. K. Rhodes, *Phys. Rev. Lett.*, **34**, 300 (1975).

(3) D. Proch and H. Schröder, *Chem. Phys. Lett.*, **61**, 426 (1979).

(4) See, for instance, R. V. Ambartsumian and V. S. Letokhov, *Acc. Chem. Res.*, **10**, 61 (1977).

(5) J. V. Tietz and S. I. Chu, *Chem. Phys. Lett.*, **101**, 446 (1983).

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discussed the semiclassical aspects of a Morse oscillator driven by a classical radiation field by formulating the matrix representation of an appropriate classical resonance Hamiltonian¹⁴⁻²¹ using WKB wave functions²² for the basis states. A uniform semiclassical "dressed state" approach is developed in the present paper that circumvents the use of a multilevel matrix treatment (e.g., ref 18) to describe the absorption of two (or more) photons. An alternative semiclassical approach for an explicitly time-dependent Hamiltonian is presented in the Appendix.

Classical Resonance Hamiltonian

The energy-conserving classical Hamiltonian for the dipole interaction of a Morse oscillator with a classical radiation field is^{13,23}

$$H = H_m(r, p) + \frac{1}{2}(P^2 + \omega^2 Q^2) - (4\pi\omega^2/V_c)^{1/2}\mu(r)Q \quad (1)$$

where P and Q are the abstract momentum and coordinate of the field, respectively, ω is the angular frequency of the field, V_c is the volume of the radiation cavity, $\mu(r)$ is the dipole moment, and H_m is the zeroth-order Hamiltonian for a Morse oscillator²⁴ with

(6) (a) For a theoretical study of HDO and related molecules, see J. S. Hutchinson, E. L. Sibert III, and J. T. Hynes, *J. Chem. Phys.*, **81**, 1314 (1984); (b) L. Halonen and M. S. Child, *J. Chem. Phys.*, **79**, 4355 (1983); G. A. Voth, R. A. Marcus, and A. H. Zewail, *J. Chem. Phys.*, **81**, 5494 (1984); J. W. Perry, D. J. Moll, A. Kuppermann, and A. H. Zewail, *J. Chem. Phys.*, **82**, 1195 (1985).

(7) (a) R. B. Walker and R. K. Preston, *J. Chem. Phys.*, **67**, 2017 (1977); (b) F. V. Bunkin and I. I. Turgov, *Phys. Rev. A*, **8**, 601 (1973); V. E. Merchant and N. R. Isenor, *IEEE J. Quantum. Electron.*, **12**, 603 (1976); F. H. M. Faisal, *Nuovo Cimento Soc. Ital. Fis. B*, **33B**, 776 (1976); L. M. Narducci, S. S. Mitra, R. A. Shatas, and C. A. Coulter, *Phys. Rev. A*, **16**, 247 (1977); I. Schek and J. Jortner, *Chem. Phys. Lett.*, **63**, 5 (1976); I. Schek, M. L. Sage, and J. Jortner, *Chem. Phys. Lett.*, **63**, 230 (1979); I. Schek, J. Jortner, and M. L. Sage, *Chem. Phys.*, **59**, 11 (1981); S. C. Leasure and R. E. Wyatt, *Chem. Phys. Lett.*, **61**, 625 (1979); *Opt. Eng.*, **19**, 46 (1980); *J. Chem. Phys.*, **73**, 4439 (1980); S. C. Leasure, K. Milfield, and R. E. Wyatt, *J. Chem. Phys.*, **74**, 6197 (1981); J. V. Moloney and F. H. M. Faisal, *J. Phys. B*, **12**, 2829 (1979); S. I. Chu, J. V. Tietz, and K. K. Datta, *J. Chem. Phys.*, **77**, 2968 (1982); T. S. Ho and S. I. Chu, *J. Chem. Phys.*, **79**, 4708 (1983); D. C. Clary, *Mol. Phys.*, **46**, 1099 (1982); S. Leasure, *Chem. Phys.*, **67**, 83 (1982); K. B. Whaley and J. C. Light, *Phys. Rev. A*, **29**, 1188 (1984); C. A. S. Lima and L. C. M. Miranda, *J. Phys. Chem.*, **88**, 3079 (1984).

(8) P. S. Dardi and S. K. Gray, *J. Chem. Phys.*, **77**, 1345 (1982); **80**, 4738 (1984).

(9) "Quantum mechanical" refers to ref 7 and 8 to the treatment of the molecular system. A standard approach, sometimes called "semiclassical", treats the field as a classical oscillator (i.e., with a well-defined phase and amplitude) and the molecule quantum mechanically. A quantum mechanical time-dependent Hamiltonian is thus used including a driving term $\mu E_0 \cos \omega t$ to describe the effect of the field on the molecule (e.g., ref 32, p 43). This treatment is known to be an excellent approximation when the number of photons in the field is large.^{11,12,32} We shall refer to this as the "time-dependent, classical radiation field" formulation.

(10) J. Lin, *Phys. Lett. A*, **70A**, 195 (1979); K. M. Christoffel and J. M. Bowman, *J. Phys. Chem.*, **85**, 2159 (1981).

(11) J. R. Stine and D. W. Noid, *J. Phys. Chem.*, **86**, 3733 (1982); D. W. Noid and J. R. Stine, *Chem. Phys. Lett.*, **65**, 153 (1979).

(12) M. J. Davis and R. E. Wyatt, *Chem. Phys. Lett.*, **86**, 235 (1982).

(13) R. B. Shirts and T. F. Davis, *J. Phys. Chem.*, **88**, 4665 (1984). This paper also contains an independent derivation of a 1:1 classical resonance Hamiltonian similar to that given by eq 10 of the text.

(14) S. K. Gray, *Chem. Phys.*, **75**, 67 (1983).

(15) B. V. Chirikov, *Phys. Rep.*, **52C**, 263 (1979), and references cited therein.

(16) E. V. Shuryak, *Sov. Phys.—JETP (Engl. Transl.)*, **44**, 1070 (1976).

(17) G. M. Zaslavsky, *Phys. Rep.*, **80C**, 157 (1981), and references cited therein.

(18) S. K. Gray, *Chem. Phys.*, **83**, 125 (1984).

(19) G. H. Walker and J. Ford, *Phys. Rev.*, **188**, 416 (1969). For reviews, see E. F. Jaeger and A. J. Lichtenberg, *Ann. Phys. N.Y.*, **71**, 319 (1972); M. Tabor, *Adv. Chem. Phys.*, **46**, 73 (1981); P. Brumer, *Adv. Chem. Phys.*, **47**, 201 (1981).

(20) R. A. Marcus, *Ann. N.Y. Acad. Sci.*, **357**, 169 (1980).

(21) T. Uzer, D. W. Noid, and R. A. Marcus, *J. Chem. Phys.*, **79**, 4412 (1983).

(22) R. A. Marcus, *Chem. Phys. Lett.*, **7**, 525 (1970).

(23) E. T. Jaynes in "Coherence and Quantum Optics", L. Mandel and E. Wolf, Eds., Plenum Press, New York, 1973; M. D. Crisp and E. T. Jaynes, *Phys. Rev. [Sect.] A*, **179**, 1253 (1969); W. H. Miller, *J. Chem. Phys.*, **69**, 2188 (1978).

displacement coordinate r and conjugate momentum p .

If a canonical transformation is made to Morse oscillator action-angle variables (I_m, θ_m) ²⁵ and to harmonic oscillator action-angle variables (I_f, θ_f) for the field, given in the latter case by $Q = (2I_f/\omega)^{1/2} \cos \theta_f$ and $P = -(2I_f\omega)^{1/2} \sin \theta_f$, eq 1 is transformed to

$$H = I_m\omega_m^0 - I_m^2\omega_m^0\chi + I_f\omega - E_0\mu(I_m, \theta_m) \cos \theta_f \quad (2)$$

where ω_m^0 and $\omega_m^0\chi$ are the harmonic angular frequency and anharmonicity, respectively, of the Morse oscillator and $E_0 = (8\pi I_f\omega/V_c)^{1/2}$ is defined as the field strength.^{11,12} The actions I_i in eq 2 are defined as the usual action variables²⁶ divided by 2π and $\hbar = 1$ throughout the present paper.

A 1:1 resonance condition^{15-17,19} exists when, for the value I_m' of the action I_m , the frequency of the Morse oscillator $\omega_m = (\partial H_m/\partial I_m)_{I_m=I_m'}$ satisfies

$$\omega_m(I_m') = \omega_m^0 - 2I_m'\omega_m^0\chi \simeq \omega \quad (3)$$

When a nonlinear coupling between oscillator modes is present and there is a near 1:1 resonance, the variable $\theta_m - \theta_f$ is a "slow" angle.^{15-17,19} By virtue of eq 3, this angle satisfies

$$\frac{d}{dt}(\theta_m - \theta_f) \simeq 0 \quad (4)$$

This condition suggests a canonical transformation^{15-17,19} such as

$$I_\alpha = 2I_m \quad I_\beta = I_m + I_f \quad (5)$$

$$2\alpha = \theta_m - \theta_f + \delta \quad \beta = \theta_f \quad (6)$$

where δ is a constant chosen as in ref 27 to ensure a real, negative contribution for the last term in eq 8 (e.g., for the linear dipole approximation used later, δ equals π). The zeroth-order Hamiltonian in the new action-angle variables becomes

$$H_0(I_\alpha, I_\beta) = I_\alpha\Omega - \omega_m^0\chi'I_\alpha^2 + I_\beta\omega \quad (7)$$

where $\Omega = (\omega_m^0 - \omega)/2$ and $\chi' = \chi/4$. The perturbation term in eq 2 $-E_0\mu(I_m, \theta_m) \cos \theta_f$ is then expanded in a complex-valued double-Fourier series in θ_m and θ_f , expressed in terms of the new angle variables α and β , and averaged over the "fast" variable β . Only the terms having the "slow angle" variable 2α will remain after this averaging,^{15-17,19} so the Hamiltonian for this 1:1 resonance system becomes

$$H = I_\alpha\Omega - \omega_m^0\chi'I_\alpha^2 + I_\beta\omega - V_0 \cos 2\alpha \quad (8)$$

where V_0 denotes $|2V_{1-1}(I_m', I_f)|$: V_{1-1} is the (1,-1) Fourier component, $-(2\pi)^{-2} \int_0^{2\pi} \int_0^{2\pi} E_0\mu(I_m', \theta_m) \cos \theta_f e^{-i(\theta_m - \theta_f)} d\theta_m d\theta_f$, evaluated at the resonance center^{15-17,19} $I_m = I_m'$ and at any I_f .

Because the angle β conjugate to the total action of the system I_β does not appear in eq 8, I_β is a constant of the motion in this approximation. The Hamiltonian (8) may then be written as

$$H = I_\beta\omega - H_R = E \quad (9)$$

where E is the total energy and H_R is a "resonance" Hamiltonian.^{15-17,19}

$$H_R = E_R = \mu_m^0\chi'I_\alpha^2 - I_\alpha\Omega + V_0 \cos 2\alpha \quad (10)$$

The quantity V_0 in eq 10, given earlier, may be rewritten as

$$V_0 = \frac{E_0}{2\pi} \int_0^{2\pi} \mu(I_m', \theta_m) e^{-i\theta_m} d\theta_m = E_0\bar{\mu} \quad (11)$$

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

(25) A canonical transformation to Morse oscillator action-angle variables, with the action defined semiclassically, for $\hbar = 1$, as $I_m = 1/2$, is given by Rankin and Miller (C. C. Rankin and W. H. Miller, *J. Chem. Phys.*, **55**, 3150 (1971)).

(26) H. Goldstein, "Classical Mechanics", Addison-Wesley, Reading, MA, 1980, p 457.

(27) G. A. Voth and R. A. Marcus, *J. Chem. Phys.*, in press.

which is simply the field strength E_0 times the fundamental Fourier component $\bar{\mu}$ of the dipole moment evaluated at the center of the resonance.

Uniform Semiclassical Approximation

The oscillator field system may be quantized by converting eq 9 into a Schrödinger equation. To do this, the I_i 's are replaced by semiclassical action operators,^{21,22} given by $(1/i) d/d\alpha + 1$ for the α motion and by $(1/i) d/d\beta + 1$ for the β motion. For a separable semiclassical basis $\psi(\alpha) \varphi(\beta)$, this procedure yields the semiclassical Schrödinger equations for $\psi(\alpha)$ and $\varphi(\beta)$

$$\frac{d\varphi}{d\beta} - i[E_\beta/\omega - 1]\varphi = 0 \quad (12)$$

where $E_\beta = I_\beta \omega$ and

$$\frac{d^2\psi}{d\alpha^2} - 2i(\xi - 1) \frac{d\psi}{d\alpha} + [A - 2q \cos 2\alpha]\psi = 0 \quad (13)$$

where

$$\xi = 2\Omega/\omega_m^0 \chi = 2I_m^r / A = [4(\Omega + E_\beta - E)/\omega_m^0 \chi] - 1 \quad q = 2V_0/\omega_m^0 \chi \quad (14)$$

Solution of eq 12 yields an equation for the (normalized) primitive semiclassical wave function²² $(2\pi)^{-1/2} \exp[i(I_\beta - 1)\beta]$. Equation 13 may be solved by defining an auxiliary function $F(\alpha)$, given by²¹

$$F(\alpha) = \exp[i(1 - \xi)\alpha]\psi(\alpha) \quad (15)$$

and introducing it into eq 13. One thus obtains Mathieu's equation^{28,29} for $F(\alpha)$

$$\frac{d^2 F(\alpha)}{d\alpha^2} + [a_\nu - 2q \cos 2\alpha]F(\alpha) = 0 \quad (16)$$

where

$$a_\nu = (\xi - 1)^2 + A \quad (17)$$

The order ν of the Mathieu equation^{28,29} is given by³⁰

$$\nu = 2I_m - \xi = 2(I_m - I_m^r) \quad (18)$$

which is, in general, not an integer. The solutions of eq 16 together with eq 12, 14, and 17 give the uniform semiclassical eigenvalues for the Hamiltonian (1) as

$$E = E_\beta + I_m^r \Omega - a_\nu \omega_m^0 \chi' \quad (19)$$

Semiclassical Dressed State Description

When the semiclassical eigenvalues of the Hamiltonian (1) as given by eq 19 are plotted as a function of the field frequency ω and at constant E_0 , they exhibit avoided crossings, as in Figure 1. The frequencies ω at which these avoided crossings occur may be obtained from the semiclassical uniform approximation formula (eq 16); namely, they occur when the orders of the Mathieu equation correspond to integers^{21,28} such that

$$\nu = -\nu' \quad (20)$$

Here, ν and ν' correspond to the two different states involved in the avoided crossing. Typically, the characteristic values a_ν and $b_{\nu'}$ of the Mathieu equation (eq 16) are associated with these states.^{21,28,29}

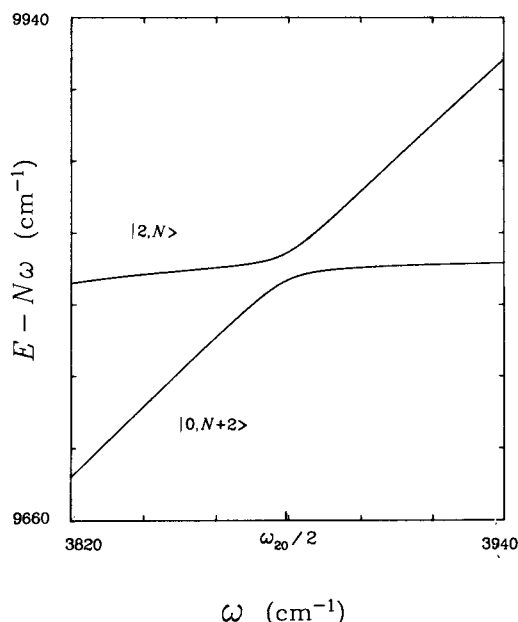


Figure 1. A semiclassical two-photon avoided crossing of the dressed states $|0, N+2\rangle$ and $|2, N\rangle$. The resonant excitation frequency $\omega_{20}/2 = 3879 \text{ cm}^{-1}$ is indicated by the location of the avoided crossing.

The interpretation of the states involved in an avoided crossing may be clarified by considering the quantum numbers associated with the zeroth-order actions

$$I_m = (n_m + 1/2) \quad I_f = N + n \\ I_m' = (n_m' + 1/2) \quad I_f' = N \quad (21)$$

where N is a very large number of "background" photons for the typical laser cavity,³¹ n is the number of photons to be absorbed ($n \ll N$), and n_m (n_m') is the quantum number of the Morse oscillator. These quantum numbers in eq 21 are associated with the zeroth-order semiclassical eigenstates,²² denoted in this section by $|n_m, N+n\rangle$ and $|n_m', N\rangle$. A further simplification may be made since N is normally so large that it may be taken as a constant, and hence the field strength $E_0 \equiv (8\pi N\omega/V_0)^{1/2}$ is constant.^{11,12,32}

For a two-level model,³³ an isolated avoided crossing²¹ of the eigenvalues indicates a zeroth-order degeneracy between the basis states (e.g., $|n_m, N+n\rangle$ and $|n_m', N\rangle$ in the present instance) at the avoided crossing. Therefore, for nonzero coupling between the field and the oscillator, the avoided crossing condition identifies the resonant excitation frequency where the Morse state $|n_m\rangle$ absorbs n photons and is excited to the state $|n_m'\rangle$.

The avoided crossing condition is given by eq 20 and is satisfied whenever ξ equals $n_m + n_m' + 1$ ²¹ or, from eq 14

$$I_m^r = (n_m + n_m' + 1)/2 \quad (22)$$

This I_m^r is seen to be the mean action $\bar{I}_m$ between the two levels undergoing the avoided crossing. Hence, eq 22 together with eq 3 indicates that, at a field frequency

$$\omega = \omega_m^0 - 2\bar{I}_m \omega_m^0 \chi \quad (23)$$

a field-induced resonance between states with Morse quantum numbers n_m and n_m' occurs. It has been noted (e.g., ref 34) that n times the classical frequency in eq 23 corresponds exactly to

(28) N. W. McLachlan, "Theory and Applications of Mathieu Functions", Clarendon Press, Oxford, 1947.

(29) M. Abramowitz and I. A. Stegun, Eds., "Handbook of Mathematical Functions", Dover, New York, 1965, Chapter 20.

(30) Since a general solution²⁸ to the zeroth-order Mathieu equation (i.e., with $q = 0$) is $\sim e^{i(k-1)\alpha}$, the zeroth-order wave function in the angle α may be written from eq 15 as $\sim e^{i(I_m-1)\alpha}$. The zeroth-order primitive semiclassical wave function²² is also $\sim e^{i(I_m-1)\alpha} = e^{2i(I_m-1/2)\alpha}$, so comparison of the two zeroth-order wave functions yields $\nu = 2I_m - \xi$ for the order of the Mathieu equation.^{28,29}

(31) The zero-point energy of the field mode is not written explicitly here since $N \gg 1/2$. For a photon energy of $\sim 1000 \text{ cm}^{-1}$, the photon densities for laser intensities 1 GW/cm^2 and 1 TW/cm^2 are $\sim 10^{18}$ photons/ cm^3 and $\sim 10^{21}$ photons/ cm^3 , respectively.

(32) R. Loudon, "Quantum Theory of Light", Clarendon Press, Oxford, 1973, Chapter 7.

(33) E.g., C. Cohen-Tannoudji, B. Diu, and F. Laloe, "Quantum Mechanics", Vol. I, Wiley, New York, 1977, Chapter IV.

(34) M. L. Koszykowski, D. W. Noid, and R. A. Marcus, *J. Phys. Chem.* **86**, 2113 (1982); J. R. Stine and D. W. Noid, *J. Chem. Phys.*, **78**, 1876 (1983).

the quantum-mechanical resonant excitation (or Bohr) frequency, $\omega_{n'm'm} \equiv E_{n'm'} - E_{n_m}$, between the two Morse oscillator levels with energies $E_{n'm'}$ and E_{n_m} .

The splittings between states at isolated avoided crossings are,^{21,28} for small enough q (the typical case in the present problem³⁵)

$$(n_m \rightarrow n_m + 1) \Delta E_1 = \frac{(a_1 - b_1)\omega_m^0 \chi}{4} = V_0 + O(q^3) \quad (24a)$$

$$(n_m \rightarrow n_m + 2) \Delta E_2 = \frac{(a_2 - b_2)\omega_m^0 \chi}{4} = \frac{V_0^2}{2\omega_m^0 \chi} + O(q^4) \quad (24b)$$

and so on for higher order transitions. One recalls from eq 11 and 22 that the V_0 's in eq 24a and 24b are functions of n_m and n'_m . When the system is initially in one of the zeroth-order states involved in the avoided crossing, the splittings ΔE_n of the eigenvalues give the characteristic Rabi frequency ω_R for oscillation between these zeroth-order states.³³ One may demonstrate this as follows:

Suppose at $t = 0$ the system is in an initial state $|\psi(0)\rangle$ that may be expressed as a linear combination of only two "exact" semiclassical wave functions $|a\rangle$ and $|b\rangle$. Due to the coupling between the field and the oscillator, this state evolves in times as

$$|\psi(t)\rangle = e^{-iH_{sc}t}|\psi(0)\rangle = C_a|a\rangle e^{-iE_a t} + C_b|b\rangle e^{-iE_b t} \quad (25)$$

where C_a equals $\langle a|\psi(0)\rangle$, C_b equals $\langle b|\psi(0)\rangle$, and H_{sc} is the semiclassical Hamiltonian (9) (expressed, as in the previous section, in terms of semiclassical action-angle operators). The probability amplitude $|\langle\psi(0)|\psi(t)\rangle|^2$ for the state $|\psi(0)\rangle$ oscillates in time as $\cos^2([E_a - E_b]t/2)$, where $E_a > E_b$. If the field frequency ω is such that the exact states $|a\rangle$ and $|b\rangle$ are at an avoided crossing, then their splitting $\Delta E_n = E_a - E_b$ is defined as the Rabi frequency ω_R .³³

When $|\psi(0)\rangle$ is taken to be the "unexcited" dressed state $|n_m, N+n\rangle$, the probability for being in the excited dressed state $|n'_m, N\rangle$ is given by³³

$$P_{n'_m n_m}(t) = |\langle n'_m, N | e^{-iH_{sc}t} | n_m, N+n \rangle|^2 \quad (26)$$

while the probability for being in the $|n_m, N+n\rangle$ is given by

$$P_{n_m n_m}(t) = |\langle n_m, N+n | e^{-iH_{sc}t} | n_m, N+n \rangle|^2 \quad (27)$$

For the present two-level model, the energy absorption⁸ $\langle E(t) \rangle - \langle E(0) \rangle$ of the Morse oscillator starting in the state $|n_m\rangle$ is given by

$$\begin{aligned} \langle \psi(t) | H_m | \psi(t) \rangle - E_{n_m} &\simeq E_{n'_m} P_{n'_m n_m}(t) + E_{n_m} [P_{n_m n_m}(t) - 1] \\ &= \omega_{n'_m n_m} P_{n'_m n_m}(t) \end{aligned} \quad (28)$$

This field-induced oscillation between zeroth-order states describes the time-varying absorption process of n photons by the Morse oscillator. It has recently been demonstrated numerically that a two-level Rabi model is a good approximation at (or close to) resonance even for large laser intensities (e.g., 44 TW/cm²).⁸

Relationship to Quantum Dressed State Theory

In the quantum dressed state picture,¹ the classical Hamiltonian in eq 1 is quantized by first replacing the classical variables (p, r, P, Q) with the quantum-mechanical operators ($\hat{p}, \hat{r}, \hat{P}, \hat{Q}$) and then solving the matrix representation of the quantum counterpart of eq 1 for the eigenvalues and eigenvectors. When plotted vs. ω , an avoided crossing of two eigenvalues of this matrix (the dressed state matrix^{1,36}) identifies, as already noted for the sem-

iclassical case, a resonant excitation frequency, and the splitting between the states at the avoided crossing is the Rabi frequency of the transition.¹ For a given field frequency ω , the correspondence of the quantum Rabi and resonant excitation frequencies with those obtained by the semiclassical treatment in the previous section may be demonstrated as follows:

To describe an isolated quantum-mechanical avoided crossing corresponding to an n -photon transition, it is convenient to transform the full dressed state matrix $\mathbf{H}$ via a Van Vleck transformation³⁷ $\mathbf{T}^{-1}\mathbf{H}\mathbf{T}$ of order k (where $k \geq n$). This transformation serves to diagonalize $\mathbf{H}$ to order k except for any zeroth-order states that are degenerate or nearly degenerate. This procedure is ideal for the present purpose of treating an isolated avoided crossing, since here one is dealing with a case where only two zeroth-order states are degenerate or nearly degenerate. Specifically, if an isolated avoided crossing between two levels, as in Figure 1, occurs in a small frequency interval $\Delta\omega$, there are only two states in that interval which are nearly degenerate amid the vast number of states in $\mathbf{H}$. The Van Vleck transformation then yields a matrix $\mathbf{G}$ that is diagonal to k th order except for a 2×2 submatrix

$$\begin{bmatrix} G_{n'm'n'm} & G_{n'm'n_m} \\ G_{n_m n'm'} & G_{n_m n_m} \end{bmatrix} = \begin{bmatrix} E_{n'_m} + N\omega & V^{(k)} \\ V^{(k)*} & E_{n_m} + (N+n)\omega \end{bmatrix} \quad (29)$$

that includes the two degenerate or nearly degenerate quantum states $|n'_m, N\rangle$ and $|n_m, N+n\rangle$. In eq 29, E_{n_m} ($E_{n'_m}$) is the energy of a quantum-mechanical Morse oscillator eigenstate $|n_m\rangle$ ($|n'_m\rangle$), $V^{(k)}$ is the perturbation coupling of order k between states, and N, n and ω are as defined previously. There are, in general, some diagonal perturbation corrections, but for realistic laser intensities (< 1 TW/cm²), they are estimated to have a negligible effect on the resonant excitation frequencies.³⁷ The contribution from the off-resonant components of the matrix $\mathbf{H}$ is shifted via the Van Vleck transformation to the coupling term $V^{(k)}$. Expressions for the coupling elements $V^{(k)}$ through third order ($k = 3$) may be found in ref 37. In general, a coupling element of at least order n is necessary to induce an n -photon transition (i.e., $V^{(k)}$, where $k < n$, would be equal to zero for the n -photon transition). Higher order terms ($k > n$) usually have a negligible contribution for such transitions, so only terms $V^{(n)}$ of n th order will be considered.³⁸

The two diagonal elements of the matrix (29) become degenerate and hence undergo an avoided crossing when $n\omega$ equals $\omega_{n'_m n_m}$. As in the semiclassical case, there is a field-induced resonant transition between Morse oscillator states $|n_m\rangle$ and $|n'_m\rangle$ at this frequency. In the previous section, n times the semiclassically calculated resonance frequency (eq 23) was stated to correspond exactly with the quantum value for $\omega_{n'_m n_m}$. This may be demonstrated by considering the quantum expression for $\omega_{n'_m n_m}$:

$$\omega_{n'_m n_m} = (n'_m - n_m)\omega_m^0 - (n'_m - n_m)(n'_m + n_m + 1)\omega_m^0 \chi \quad (30)$$

(37) The Van Vleck transformation is given, for example, in J. E. Wollrab, "Rotational Spectra and Molecular Structure", Academic Press, New York, 1967, Appendix 7. In the matrix (29), the diagonal self-energy corrections for the typical Morse oscillator had a negligible effect on the resonant excitation frequencies for the system treated and have been neglected (e.g., for a laser intensity of 1 TW/cm², the one- and two-photon peaks for HF show virtually no shifts from the expected zero-order Morse oscillator resonant excitation frequencies⁸). A modified version of the Van Vleck transformation has been used recently to treat two-state systems in quantized fields (P. K. Aravind and J. O. Hirschfelder, *J. Phys. Chem.*, **88**, 4788 (1984)).

(38) For the perturbation $V = -4\pi\omega^2/V_0^{1/2}\mu(r)Q$ in eq 1, the quantum one- and two-photon matrix elements are given at resonance by $V^{(1)} = \langle n'_m, N | V | n_m, N+1 \rangle$ and

$$V^{(2)} = \sum_j \sum_p \frac{\langle n'_m, N | V | p, j \rangle \langle p, j | V | n_m, N+2 \rangle}{(N+2-j)\omega - \omega_{p n_m}}$$

respectively. The summations in the latter case are over the photon states $|j\rangle$ and Morse oscillator states $|p\rangle$, excluding those appearing in the diagonal elements of eq 29. The equality at resonance $2\omega = \omega_{n'_m n_m}$ has been used here to simplify the expression for $V^{(2)}$ in ref 37. For the general case of the field tuned slightly off-resonance from the two-photon transition frequency $\omega_{n'_m n_m}$, $V^{(2)}$ is given by the above expression with an added multiplicative factor $(d_{pj} + \Delta/2)/(d_{pj} + \Delta)$, where d_{pj} is the denominator term from above and Δ is defined as $\omega_{n'_m n_m} - 2\omega$.

(35) For HF Morse parameters^{7a} and a laser intensity of 1 TW/cm²,¹⁸ the expansions for a_i and b_i in ref 28, p 16, are found to be rapidly convergent.

(36) This matrix is defined as the matrix representation of the Hamiltonian (1) using the quantum "dressed state" basis¹ $|p, j\rangle$, where $|p\rangle$ and $|j\rangle$ denote a Morse oscillator eigenstate with quantum number p and a harmonic oscillator photon state with occupation number j , respectively.

TABLE II: Quantum $\langle n_m+2|r|n_m+1\rangle\langle n_m+1|r|n_m\rangle$ vs. Semiclassical $[\tilde{r}(\bar{I}_m)]^2$

n_m	$\langle n_m+2 r n_m+1\rangle\langle n_m+1 r n_m\rangle$	$[\tilde{r}(\bar{I}_m)]^2$
0	0.0222	0.0235
1	0.0393	0.0401
2	0.0568	0.0574
3	0.0750	0.0755
4	0.0940	0.0945
5	0.1139	0.1143

For the 1:1 resonance, this is simply $n\omega$, where ω is the classical frequency in eq 23 and n equals $n'_m - n_m$.

At the resonant field frequency, the matrix (29) yields the time-dependent Rabi flopping formula³³ $\sim \sin^2(\omega_R t/2)$ for the probability of being in the dressed Morse oscillator state $|n'_m, N\rangle$ after starting in dressed state $|n_m, N+n\rangle$, where the quantum Rabi frequency ω_R for n photon absorption equals $2|V^{(n)}|$.³³ It is seen from eq 24a, 24b, and 29 that, at resonance, the semiclassically calculated Rabi frequency ΔE_n is to be compared, in this approximation, to the quantum Rabi frequency $2|V^{(n)}|$. These quantities are now considered for two specific cases:

(a) *One-Photon Absorption.* The semiclassical one-photon Rabi frequency is given by eq 24a as $E_0\tilde{\mu}$, whereas the quantum one-photon Rabi frequency is given by³⁹ $E_0\langle n'_m|\hat{\mu}|n_m\rangle$ with n'_m equal to $n_m + 1$. In this case, the Morse oscillator matrix element $\langle n'_m|\hat{\mu}|n_m\rangle$ appearing in the quantum-mechanical quantity $V^{(1)}$ is to be compared with the fundamental Fourier component $\tilde{\mu}$ (cf. eq 11) evaluated at the mean action $\bar{I}_m = n_m + 1$ for the one-photon transition. The same semiclassical Rabi frequency for one-photon absorption in terms of a Fourier component has been obtained by a somewhat different argument.¹⁸ These Fourier components have recently been shown to give excellent agreement with the quantum matrix elements for Morse^{34,40} and other^{40,41} oscillators. By use of HF Morse parameters^{7a} and a linear dipole approximation, values of $\langle n_m+1|\hat{\mu}|n_m\rangle$ and $\tilde{r}(\bar{I}_m)$ are calculated and compared in Table I.

(b) *Two-Photon Absorption.* The semiclassical two-photon Rabi frequency is given by eq 24b as $(E_0\tilde{\mu})^2/2\omega_m^0\chi$. For this case, $\tilde{\mu}$ is the fundamental Fourier component of the dipole moment function evaluated at the mean action $\bar{I}_m = (2n_m + 3)/2$ for the two-photon transition between the Morse states $|n_m\rangle$ and $|n_m+2\rangle$. It is clear that the semiclassical two-photon Rabi frequency has the proper dependence on the field strength⁴² unlike the two-level model in a previous semiclassical study.¹⁸ Moreover, this quantity is inversely dependent on $\mu_m^0\chi$, reflecting the detuning of the two-photon resonance by the Morse anharmonicity.

To demonstrate the correspondence of the semiclassical Rabi frequency with the quantum result, the quantum two-photon coupling element $V^{(2)}$ is examined. This coupling term for the resonant field frequency $2\omega = \omega_{n'_m n_m}$, where $n'_m = n_m + 2$, and for large N is given by⁴³

$$V^{(2)} = \frac{E_0^2}{4} \sum_p \left[\frac{\langle n_m+2|\hat{\mu}|p\rangle\langle p|\hat{\mu}|n_m\rangle}{\omega - \omega_{pn_m}} \right] \quad (31)$$

with E_0 being a constant. If one uses the resonance condition (eq 23) and notes that the term with $\langle n_m+2|\hat{\mu}|n_m+1\rangle\langle n_m+1|\hat{\mu}|n_m\rangle$ is the dominant contribution to the sum over Morse states $|p\rangle$,⁴⁴ the

(39) From footnote 38, $V^{(1)}$ is given by $-(4\pi\omega^2/V_c)^{1/2}\langle n'_m|\hat{\mu}|n_m\rangle\langle N|Q|N+1\rangle$. If harmonic oscillator selection rules are used for the field mode, this expression reduces to $-(8\pi(N+1)\omega/V_c)^{1/2}\langle n'_m|\hat{\mu}|n_m\rangle/2$. Since $N \gg 1$ and N equals I_f , $V^{(1)}$ may be written as $-E_0\langle n'_m|\hat{\mu}|n_m\rangle/2$, where $E_0 = (8\pi I_f\omega/V_c)^{1/2}$ as in the text.

(40) D. M. Wardlaw, private communication.

(41) D. M. Wardlaw, D. W. Noid, and R. A. Marcus, *J. Phys. Chem.*, **88**, 536 (1984).

(42) E.g., T. Oka and T. Shimizu, *Phys. Rev. A*, **2**, 587 (1970), and references cited therein.

(43) From footnote 38, the summation over the field states $|j\rangle$ in the expression for $V^{(2)}$ has only one nonzero term (i.e., for $|j\rangle = |N+1\rangle$). Since each numerator term reduces to $E_0^2\langle n'_m|\hat{\mu}|p\rangle\langle p|\hat{\mu}|n_m\rangle/4$ (cf. footnote 39), the summation is then given by eq 31.

quantum two-photon Rabi frequency is given approximately by

$$2|V^{(2)}| \simeq \frac{E_0^2}{2\omega_m^0\chi} \langle n_m+2|\hat{\mu}|n_m+1\rangle\langle n_m+1|\hat{\mu}|n_m\rangle \quad (32)$$

From eq 24b and 32, the agreement between the semiclassical and quantum Rabi frequencies is expected to be good if

$$[\tilde{\mu}(\bar{I}_m)]^2 \simeq \langle n_m+2|\hat{\mu}|n_m+1\rangle\langle n_m+1|\hat{\mu}|n_m\rangle \quad (33)$$

A comparison of these two quantities for HF and a linear dipole approximation is given in Table II.

Adaptation to a Polyatomic Molecule

For a nonrotating polyatomic molecule in a radiation field, it is assumed that the Hamiltonian may be written as

$$H = H_0(\mathbf{I}) + I_f\omega - E_0\mu(\mathbf{I},\theta) \cos \theta_f \quad (34)$$

Here, I_f and θ_f refer to the radiation field as before, and the $(\mathbf{I},\theta)$ form a set of "good" action-angle variables describing perhaps Morse-like vibrational modes with no internal resonances.^{15,19} These variables may be obtained, for instance, by perturbative or other approximate methods. If there is a resonance between the field and some vibrational frequency $\omega_m = \partial H_0/\partial I_m$ of the molecule, I_m being the m th action with conjugate angle θ_m , then the angle variable $\theta_m - \theta_f$ becomes a "slow" angle. If the Hamiltonian H in eq 34 is averaged over all molecular angle variables θ_i except θ_m and if H_0 can be expanded in a Taylor series in I_m about $I_m = 0$, one obtains

$$H = H_m(I_m, \mathbf{I}') + I_f\omega - E_0\tilde{\mu}(\mathbf{I}, \theta_m) \cos \theta_f + H'_0(\mathbf{I}') \quad (35)$$

where $H'_0(\mathbf{I}')$ is a constant term for the set of actions $\mathbf{I}'$ excluding I_m . If H_m is truncated at a quadratic function of I_m (which may depend on $\mathbf{I}'$), the Hamiltonian in eq 35 has the form of eq 2, but ω_m^0 now denotes $(\partial H_0/\partial I_m)_{I_m=0}$ and $\omega_m^0\chi$ denotes $1/2(\partial^2 H_0/\partial I_m^2)_{I_m=0}$.

Discussion

A semiclassical treatment of one- and two-photon absorption by a Morse oscillator has been presented in this paper that has a direct correspondence with the quantum-mechanical dressed state approach. The use of the Mathieu function uniform approximation allows one to calculate the Rabi and resonant excitation frequencies directly from eq 23–24b without the use of a multistate matrix treatment. For this reason, the present uniform semiclassical method is useful for characterizing multiphoton absorption processes in a simple way. In addition, it has been noted¹⁸ that, for realistic laser intensities (<1 TW/cm²), two-photon absorption may correspond to a nonclassical path. (More specifically, classical calculations⁸ have shown no two-photon absorption.) This fact indicates the usefulness of an appropriate uniformization procedure to treat such a process purely semiclassically, for such a uniform approximation permits quantum-mechanical tunneling.

It has been noted¹⁸ that the solutions of the Mathieu equation (eq 16) contain contributions from unphysical "states" corresponding to negative quantum numbers. This problem arises whenever primitive semiclassical wave functions in an (approximate) action-angle representation²² are used. In the case of an oscillator, one usually omits, by fiat, states with negative principal quantum numbers. In the present case, however, these "states" are distant in energy and found not to have a significant contribution. A similar situation would occur in other uses of Mathieu functions, e.g., in a description of molecular Fermi resonances.²⁷

The uniform semiclassical technique presented in this paper is not applicable in the regime of overlapping classical reso-

(44) Including only the nearly resonant term for the dressed state $|n_m+1, N+1\rangle$ (cf. footnote 36) is similar to making the rotating wave approximation (RWA). For a discussion of the usual RWA, see ref 48. A discussion of the RWA in relation to dressed state theory is given in ref 1, p 18. Using the parameters for HF given in ref 7a and a laser intensity of 1 TW/cm², we found the neglected terms in the summation (eq 31) to contribute less than 5% to the Rabi frequency.

nances^{15-17,19,20} and/or overlapping avoided crossings (e.g., ref 20). When there are overlapping classical resonances, the dynamics are thought to be chaotic classically,^{15-17,19,20} and when there are overlapping avoided crossings, the system may in some sense be regarded as quantum mechanically chaotic (e.g., ref 20). One could use, however, a multilevel semiclassical matrix treatment¹⁸ when a simple two-level treatment is not applicable.

The uniform semiclassical method allows one to calculate the absorption probabilities using the Fourier components of the dipole moment function, some of which exist in analytic form.^{40,45} In some cases, this may be preferable to calculating the more complicated quantum dipole matrix elements for the Morse oscillator.⁴⁶ When not determined analytically, the Fourier components for any general dipole moment function may be found numerically by integrating a classical trajectory with the appropriate mean action as an initial condition and then calculating the power spectrum of $\mu(t)$.^{34,41,47}

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Appendix: An Alternative Semiclassical Approach

It has been noted¹¹⁻¹³ that the time-independent²³ and time-dependent, classical radiation field⁹ formulations of the molecule-field Hamiltonian are equivalent when the number of photons N is large. For completeness, we derive here the semiclassical Schrödinger equation (eq 13) starting from the time-dependent, classical radiation field point of view.

The time-dependent Hamiltonian for the interaction of a Morse oscillator with a classical radiation field is given by⁹

$$H(r,p,t) = H_m(r,p) - E_0\mu(r) \cos \omega t \quad (\text{A1})$$

where $H_m(r,p)$ is the Morse oscillator Hamiltonian in terms of the displacement coordinate r and its conjugate momentum p . Written in Morse oscillator action-angle variables (I_m, θ_m) ,²⁵ eq A1 becomes

$$H(I_m, \theta_m, t) = I_m \omega_m^0 - I_m^2 \omega_m^0 \chi - E_0 \mu(I_m, \theta_m) \cos \omega t \quad (\text{A2})$$

The formulation of the resonance Hamiltonian for the 1:1 resonance is performed in two steps. First, the $V = -E_0\mu(I_m, \theta_m) \cos \omega t$ perturbation term is expanded in a Fourier series in θ_m , the result is expressed in terms of the "slow" angle variable $\theta_m - \omega t$ and averaged over all remaining functions of θ_m . Second, the time-dependent canonical transformation

$$I_\alpha = 2I_m \quad 2\alpha = \theta_m - \omega t + \delta \quad (\text{A3})$$

is introduced to yield a new set of action-angle variables (I_α, α) appropriate for the 1:1 resonance. This transformation is generated by the F_2 -type generating function (e.g., ref 18 and ref 26, p 383)

$$F_2 = I_\alpha(\theta_m - \omega t + \delta)/2 \quad (\text{A4})$$

and thus gives the new Hamiltonian K from the expression

$$K = H(I_\alpha, \alpha, t) + \partial F_2 / \partial t \quad (\text{A5})$$

The new Hamiltonian K now given by

$$K = I_\alpha(\omega_m^0 - \omega)/2 - I_\alpha^2 \omega_m^0 \chi / 4 - V_0 \cos 2\alpha \quad (\text{A6})$$

where V_0 is the same as in eq 11 of the text. Using the definitions of Ω and χ' given previously, we can write the resonance Hamiltonian as

$$H_R = -K = \omega_m^0 \chi' I_\alpha^2 - I_\alpha \Omega + V_0 \cos 2\alpha \quad (\text{A7})$$

which is identical with eq 9 of the text minus the constant $I_\beta \omega$ term. Gray¹⁸ has obtained a very similar, but not identical (because of the use of a slightly different canonical transformation), resonance Hamiltonian.

As in the text, introduction of the semiclassical action operator $(1/i) d/d\alpha + 1$ into eq A7 yields eq 13. As a result, both the time-dependent, classical radiation field and time-independent formulations yield the same uniform semiclassical Mathieu equation and hence the same semiclassical resonant and Rabi frequencies.

The direct correspondence of the time-independent semiclassical formulation with the quantum dressed state theory is presented in the text. The time-dependent, classical radiation field Hamiltonian (A1) may be converted to a time-independent Floquet matrix⁴⁹ that is formally equivalent^{49,50} to the quantum dressed state matrix when N is large. The language of avoided crossings may then be used in relation to the so-called quasi-energies⁵⁰ of this Floquet matrix.

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