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Multiphoton Processes in Homopolar Diatomic Molecules

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Within the framework of time-dependent perturbation theory and the Born–Oppenheimer approximation, general expressions are derived for the cross sections of multiphoton processes induced by radiation acting on a homopolar diatomic molecule. A Morse-type model of potential-energy curves of excited electronic states is proposed which gives a good representation of true curves. The procedure used to evaluate the sums over intermediate states is described. The method is based on the use of the internuclear potential Green's functions obtained in closed form. Analytic expressions are derived for one-photon and two-photon cross sections. The results for higher-order processes are presented in a form which is convenient for numerical computation. As an illustration, the cross section for one-photon dissociation of H_2^+ from the $v=0$ vibrational level is calculated as a function of wavelength. A comparison of cross sections calculated using the Morse-type model of potential curves with those using accurate wave functions of H_2^+ shows a good precision of the model.

I. INTRODUCTION

The interaction of laser radiation with atoms has been the subject of a large number of recent theoretical papers. Most of these concern the multiphoton atomic transitions corresponding to simultaneous absorption or emission of several photons by the atom and are generally treated within the framework of time-dependent perturbation theory.

In this paper, we shall present an approach for the treatment of many-photon problems in a homopolar diatomic molecule. Sections II and III contain explicit formulas for the multiphoton-dissociation and -excitation cross sections obtained within the Born–Oppenheimer approximation. The angular parts of the Nth-order matrix elements have been calculated and the selection rules for electronic transitions are given. The chief difficulty in calculating the radial parts of the Nth-order matrix elements stands in the correct evaluation of the $N-1$ summations over intermediate states. Each of these sums is extended over complete sets of vibrational states of all intermediate electronic states allowed by the selection rules.

For a given electronic state the summation over its complete vibrational spectrum may be explicitly carried out through the Green's function of the internuclear potential. In a previous paper[1] a method has been presented for calculating radial matrix elements of two-photon vibrational transitions. This method can be generalized to calculate the sums over complete sets of vibrational states in the matrix elements of multiphoton electronic transitions.

Thus, we may deduce that the construction of the potential-energy-curve model for a number of electronic states of the molecule must play an important part in these considerations. It is common for the true potential curve to be fitted to empirical expressions and we shall use the Morse potential

$$V_0(r)=D_0\left(e^{-2\alpha(r-r_0)}-2e^{-\alpha(r-r_0)}\right)$$

for the potential curve of the ground electronic state $|0\rangle$. For the potential-energy curves of excited electronic states $|i\rangle$ let us use the potentials

$$V_i(r)=D_i\left(e^{-2\alpha(r-r_0)}-2t_i\,e^{-\alpha(r-r_0)}\right)+Q_i\ .$$

This potential-energy model gives a good representation of the true repulsive ($t_i<0$) and attractive ($t_i>0$) potential curves for some homopolar diatomics (see Fig. 1).

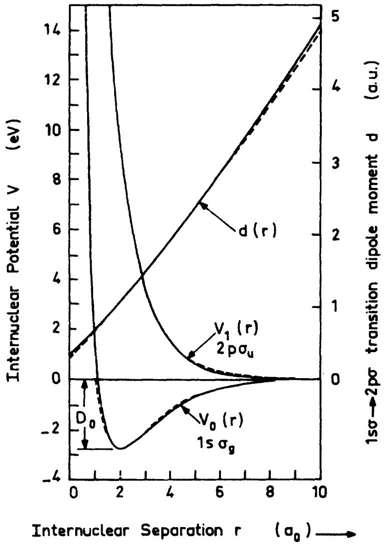

FIG. 1. Potential curves for $1s\sigma_g$ and $2p\sigma_u$ states of H_2^+ and $1s\sigma_g \rightarrow 2p\sigma_u$ transition dipole moment. The solid curves show the true potential curves of H_2^+ (Ref. 13) and the $1s\sigma_g$-$2p\sigma_u$ transition dipole moment calculated in Ref. 14 using accurate wave functions. The dashed curves for $V_0(r)$ and for $V_1(r)$ represent, respectively, the Morse potential (17) with $r_0=2a_0$, $\alpha=0.72a_0^{-1}$, $D_0=2.79$ eV, and the potential (18) with $D_t=D_0$, $t=-1.11$, $Q=0$. The dashed curve for dipole moment $d(r)$ is calculated from Eq. (33) with $d(r_0)=1.07ea_0$, $d'(r_0)=0.396e$, $x=-0.055$.

Section IV contains vibrational wave functions and Green's functions obtained in closed form for this Morse-type model. Section V gives the simple model describing the electronic-transition dipole moment. The latter enables a correct description of the dipole moments to be given in the vicinity of the internuclear equilibrium distance r_0 as well as for large r.

The evaluation of the Nth-order radial matrix elements containing many infinite summations over intermediate states is described in Sec. VI. The sums over vibrational states of each intermediate-electron term may be carried out through straightforward integrations of expressions involving the Green's functions of corresponding potential curves. Generally, this procedure requires numerical computations and will be treated in following papers. Without going into the problem of numerical integration it may be noted that one- and two-photon cross sections are obtained in analytic forms.

In Sec. VII, simple formulas are given for the cross sections of one-photon vibronic transitions. An interesting feature of the result lies in the possibility of analytically revealing the dependence of the cross section on the electric anharmonicity of the transition. In order to check the precision of the model developed in the paper, the photodissociation of H_2^+ from the $v=0$ vibrational level is considered. The results obtained are compared with those using accurate wave functions and show a high precision of the model.

In Sec. VIII an analytic expression is derived for two-photon transition cross sections. In this case, the final expression is more complicated and requires the calculation of slowly converging generalized hypergeometric series. However, the numerical operating of these series causes no difficulty.

II. MULTIPHOTON-DISSOCIATION CROSS SECTION

In the dipole approximation the nonrelativistic interaction Hamiltonian between the plane electromagnetic wave and a molecule has the form $\mathcal{E}_0 \vec{\epsilon}\cdot\vec{d}\cos\omega t$, where $\mathcal{E}_0$ is the amplitude, ω is the frequency, $\vec{\epsilon}$ is the unit polarization vector of the radiation, and $\vec{d}=\sum e_i \vec{r}_i$ is the total dipole-moment operator for the molecule. The multiphoton-dissociation probability per unit time may be determined in the Nth-order perturbation theory and is given by

$$dw=\frac{2\pi}{\hbar}\left|\left(\frac{\mathcal{E}_0}{2}\right)^N \sum_{i_1,i_2,\ldots,i_{N-1}} \frac{\langle f|\vec{\epsilon}\vec{d}|i_{N-1}\rangle\langle i_{N-1}|\vec{\epsilon}\vec{d}|i_{N-2}\rangle\cdots\langle i_1|\vec{\epsilon}\vec{d}|0\rangle}{[E_0-E_{N-1}+(N-1)\hbar\omega]\ldots(E_0-E_1+\hbar\omega)}\right|^2 d\rho\ . \tag{1}$$

The final density of states $d\rho$ appearing in Eq. (1) is $d\rho=mp\,d\Omega/(2\pi\hbar)^3$, where m and p are the reduced mass and momentum, respectively, of the dissociating particules, and $d\Omega$ is an element of the solid angle. In Eq. (1), E_0 and E_i denote the energies of the initial state $|0\rangle$ and intermediate state $|i\rangle$, respectively; $|f\rangle$ is the final-state wave function. Summation over each intermediate state $|i\rangle$ in Eq. (1) is carried out over the complete set of molecular states.

Dividing the transition probability (1) by the photon flux density $F=I/\hbar\omega$, where $I=c\mathcal{E}_0^2/8\pi$ is the intensity of the incident radiation, and summing over the initial M degeneracy we obtain an expression for the differential cross section,

$$\frac{d\sigma}{d\Omega}=\frac{\alpha}{2\pi}m\left(\frac{I}{I_0}\right)^{N-1}a_0^2E_p\,q\ \frac{1}{2K+1}\sum_{M=-K}^{K}\left|\sum_{i_1,i_2,\ldots,i_{N-1}}\frac{\langle f|\vec{\epsilon}\vec{d}|i_{N-1}\rangle\langle i_{N-1}|\vec{\epsilon}\vec{d}|i_{N-1}\rangle\ldots\langle i_1|\vec{\epsilon}\vec{d}|0\rangle}{[E_0-E_{N-1}+(N-1)E_p]\ldots(E_0-E_1+E_p)}\right|^2 . \tag{2}$$

Here $d\sigma/d\Omega$ is in cm^2/sr, $\alpha = e^2/\hbar c$ is the fine-structure constant, a_0 is the Bohr radius, I is the incident intensity in W/cm^2, and I_0 is 14.038×10^{16} W/cm^2. The photon energy E_p, the wave number of separating particles $q = p/\hbar$, and the remaining quantities in Eq. (2) are expressed in atomic units.

We assume the usual separability of the wave functions (Born–Oppenheimer), so that the molecular wave functions can be expressed as a product of electronic (φ) and nuclear (ξ) wave functions $\Psi = \varphi\,\xi$. For singlet terms of a diatomic molecule, we have[2]

$$\Psi_{n\Lambda vKM}(\vec{r}_i, \vec{r}) = \varphi_{n\Lambda K}(\xi_i, \eta_i, \zeta_i; r) \times R_{n\Lambda vK}(r)\,\Theta_{\Lambda KM}(\theta)\,\frac{e^{iM_\varphi}}{(2\pi)^{1/2}}\ ; \tag{3}$$

$\Psi(\vec{r}_i, \vec{r})$ is the wave function of a state with definite values of the absolute value K and z component M of the total angular momentum of the molecule, and a definite value Λ of the ζ component of the electron angular momentum; v are the vibrational quantum numbers and n denotes the assembly of the remaining quantum numbers which determine the state of the molecule. The variables $\vec{r}_i$ in Eq. (3) are the radius vectors of the electrons relative to the center of mass of the molecule and $\vec{r}$ is the radius vector between the nuclei. The polar angle θ and the azimuthal angle φ of the axis of the molecule are determined relative to a fixed system of coordinates x, y, and z. Besides the fixed system we have introduced a moving system of coordinates ξ, η, and ζ, with the same origin, the ζ axis directed along the axis of the molecule.

The function $\varphi_{n\Lambda K}$ in Eq. (3) is the electron wave function, depending on r as a parameter, and $R_{n\Lambda vK}(r)$ is the radial part of the nuclear wave function which satisfies the one-dimensional Schrödinger's equation with the $|n\Lambda\rangle$-electron-term potential energy. The functions $\Theta_{\Lambda MK}(\theta)$ are[2]

$$\Theta_{\Lambda MK} = i^K\left(\frac{(2K+1)\,(K+M)!}{(K+\Lambda)!\,(K-\Lambda)!\,(K-M)!}\right)^{1/2} \times \frac{(1-\cos\theta)^{(\Lambda-M)/2}}{(1+\cos\theta)^{(\Lambda+M)/2}} \times\left(\frac{\partial}{\partial(\cos\theta)}\right)^{K-M}(1-\cos\theta)^{K-\Lambda}\,(1+\cos\theta)^{K+\Lambda}\ .$$

For $\Lambda = 0$, the angular parts of the nuclear wave functions become ordinary normalized spherical harmonics $Y_{KM}(\theta, \varphi)$.

The nuclear wave function $\xi_f(\vec{r})$ of the final state $|f\rangle$ of the molecule describes a stationary state of dissociating particles, there being at infinity a plane wave propagated in a definite direction and an incoming spherical wave. The proper boundary conditions for scattering being satisfied, the continuum wave function may be expressed

$$\xi_f(\vec{r}) = (\tfrac{1}{2}\pi)^{1/2}\,q^{-1}\sum_{K_f}(2K_f+1)\,i^{K_f}\,e^{-i\delta_{K_f}} \times P_{K_f}(\cos\theta_0)\,R_{qK_f}(r)\ , \tag{4}$$

where $P_K(\cos\theta_0)$ are ordinary Legendre polynomials, $\cos\theta_0 = \vec{q}\cdot\vec{r}/qr$, θ_0 being the angle between the direction of the axis of the molecule and the momentum of the relative motion of separating particles. The function $R_{qK_f}(r)$ in Eq. (4) is the regular solution of the Schrödinger's equation with the potential energy of the final electronic state $|n_f\Lambda_f\rangle$ and for the positive eigenenergy. The asymptotic expression for R_q, when r is large, is of the form

$$R_{qK_f}(r) \approx (2/\pi)^{1/2}(1/r)\sin(qr - \tfrac{1}{2}\pi K_f + \delta_{K_f})\ , \tag{5}$$

where δ_{K_f} is the phase shift; $R_q(r)$ are normalized by the condition

$$\int_0^\infty R_{q'}(r)\,R_q(r)\,r^2 = \delta(q'-q)\ .$$

Use of the addition theorem for spherical harmonics gives us

$$\xi_f(\vec{r}) = \frac{(8\pi^3)^{1/2}}{q}\sum_{K_f}\sum_{M=-K_f}^{K_f}(i)^{K_f}\,e^{-i\delta_{K_f}} \times Y^*_{K_fM}(\theta, \varphi)\,Y_{K_fM}(\Theta, \Phi)\,R_{qK_f}(r)\ , \tag{6}$$

where Θ is the polar angle and Φ is the azimuthal angle of the wave vector $\vec{q}$ of the dissociating particles relative to the fixed axes.

Using in Eq. (2) the molecular wave functions of the initial, intermediate, and final states in the form of the products of electronic (φ) and nuclear (ξ) wave functions, let us first consider the matrix elements of the dipole moment $\vec{d}$ of the molecule in the system of coordinates ξ, η, and ζ, which rotates with the molecule (the ζ axis coinciding with the axis of the molecule). It is known[2] that the matrix elements

$$(\vec{d})_{n\Lambda}^{n'\Lambda'} = \int \varphi^*_{n'\Lambda'}\,\vec{d}\,\varphi_{n\Lambda}\,d\tau_e$$

that are not zero are

$$(d_\zeta)_{n'\Lambda}^{n\Lambda}\ ;\ (d_\xi + id_\eta)_{n'\Lambda-1}^{n\Lambda}\ ;\ (d_\xi - id_\eta)_{n'\Lambda}^{n\Lambda-1}\ . \tag{7}$$

(We denote by n the assembly of quantum numbers for the electron term, with the exception of Λ.)

It is seen from Eq. (7) that there are matrix elements diagonal with respect to Λ only for the component along the axis of the molecule ("parallel" transitions); where Λ varies by one unit, only the components perpendicular to the axis will not be zero ("perpendicular" transitions).[3]

The matrix elements (7) are related to the matrix elements $\langle n\Lambda KM|\vec{\epsilon}\cdot\vec{\mathrm{d}}|n'\Lambda'K'M'\rangle$ of the components of the same vector $\vec{\mathrm{d}}$ in a fixed system of coordinates (we assume that the polarization vector $\vec{\epsilon}$ is along the z axis).

Substituting Eq. (3) for the initial- and intermediate-singlet-state wave functions and using the continuum wave function (6) as the nuclear wave function of the final state, let us represent the sums over intermediate states $|i_1\rangle$, $|i_2\rangle, \ldots, |i_{N-1}\rangle$ in Eq. (2) in the following form:

$$\sum_{i_1,\ldots,i_{N-1}} \frac{\langle f|\vec{\epsilon}\vec{\mathrm{d}}|i_{N-1}\rangle\langle i_{N-1}|\vec{\epsilon}\vec{\mathrm{d}}|i_{N-2}\rangle\cdots\langle i_1|\vec{\epsilon}\vec{\mathrm{d}}|0\rangle}{[E_0-E_{N-1}+(N-1)E_p]\ldots(E_0-E_1+E_p)} = \frac{(2\pi)^{3/2}}{q}(-i)^{K_f}e^{i\delta_{K_f}}\,Y^*_{K_fM}(\Theta,\Phi)$$

$$\times \sum_{(n\Lambda K)_1\ldots(n\Lambda K)_{N-1}} \{\delta(\Lambda_1,\Lambda)[A(K)\delta(K_1,K)+A_+(K)\delta(K_1,K+1)+A_-(K)\delta(K_1,K-1)]$$

$$+\delta(\Lambda_1,\Lambda-1)[B(K)\delta(K_1,K)+B_+(K)\delta(K_1,K+1)+B_-(K)\delta(K_1,K-1)]$$

$$+\delta(\Lambda_1,\Lambda+1)[C(K)\delta(K_1,K)+C_+(K)\delta(K_1,K+1)+C_-(K)\delta(K_1,K-1)]\}$$

$$\times\{\delta(\Lambda_2,\Lambda_1)[A(K_1)\delta(K_2,K_1)+A_+(K_1)\delta(K_2,K_1+1)+A_-(K_1)\delta(K_2,K_1-1)]$$

$$+\delta(\Lambda_2,\Lambda_1-1)[B(K_1)\delta(K_2,K_1)+B_+(K_1)\delta(K_2,K_1+1)+B_-(K_1)\delta(K_2,K_1-1)]$$

$$+\delta(\Lambda_2,\Lambda_1+1)[C(K_1)\delta(K_2,K_1)+C_+(K_1)\delta(K_2,K_1+1)+C_-(K_1)\delta(K_2,K_1-1)]\}$$

$$\cdots\{\delta(\Lambda_f,\Lambda_{N-1})[A(K_{N-1})\delta(K_f,K_{N-1})+A_+(K_{N-1})\delta(K_f,K_{N-1}+1)+A_-(K_{N-1})\delta(K_f,K_{N-1}-1)]$$

$$+\delta(\Lambda_f,\Lambda_{N-1}-1)[B(K_{N-1})\delta(K_f,K_{N-1})+B_+(K_{N-1})\delta(K_f,K_{N-1}+1)+B_-(K_{N-1})\delta(K_f,K_{N-1}-1)]$$

$$+\delta(\Lambda_f,\Lambda_{N-1}+1)[C(K_{N-1})\delta(K_f,K_{N-1})+C_+(K_{N-1})\delta(K_f,K_{N-1}+1)+C_-(K_{N-1})\delta(K_f,K_{N-1}-1)]\}$$

$$\times M(n_1\Lambda_1K_1, n_2\Lambda_2K_2,\ldots,n_f\Lambda_fK_f|E_p)\ . \tag{8}$$

Here $\Lambda_f=0$; $\delta(\Lambda,\Lambda')$, $\delta(K,K')$ are the Kronecker symbols, which express the selection rules $\Delta\Lambda=0$, ±1; $\Delta K=0$, ±1 for each intermediate transition. Each of the $N-1$ summations in Eq. (8) is carried out over all electron terms $|n\Lambda\rangle$ allowed by the $\Delta\Lambda=0$, ±1 selection rule and (for a given electron term) over rotational quantum number K, allowed by the $\Delta K=0$, ±1 selection rule. The coefficients A, B, and C in Eq. (8) represent the results of the N integrations over angular variables θ and φ and can be obtained using the standard relationships[4] between the matrix elements in the rotating and fixed systems of coordinates:

$$A(K)=\frac{\Lambda M}{K(K+1)}\ ,\quad A_+(K)=-\frac{i}{K+1}\left(\frac{[(K+1)^2-M^2][(K+1)^2-\Lambda^2]}{4(K+1)^2-1}\right)^{1/2},\quad A_-(K)=\frac{i}{K}\left(\frac{(K^2-M^2)(K^2-\Lambda^2)}{4K^2-1}\right)^{1/2};$$

$$B(K)=\frac{M}{2K(K+1)}[(K+\Lambda)(K-\Lambda+1)]^{1/2},\quad B_+(K)=\frac{1}{2(K+1)}\left(\frac{(K+1-\Lambda)(K+2-\Lambda)[(K+1)^2-M^2]}{(2K+1)(2K+3)}\right)^{1/2},$$

$$B_-(K)=-\frac{1}{2K}\left(\frac{(K+\Lambda)(K+\Lambda-1)(K^2-M^2)}{4K^2-1}\right)^{1/2};$$

$$C(K)=\frac{M}{2K(K+1)}[(K+\Lambda+1)(K-\Lambda)]^{1/2}\ ,\quad C_+(K)=-\frac{1}{2(K+1)}\left(\frac{(K+\Lambda+2)(K+1+\Lambda)[(K+1)^2-M^2]}{(2K+1)(2K+3)}\right)^{1/2},$$

$$C_-(K)=\frac{1}{2K}\left(\frac{(K-\Lambda-1)(K-\Lambda)(K^2-M^2)}{4K^2-1}\right)^{1/2} \tag{9}$$

In the case of parallel transitions ($\Delta\Lambda = 0$) only terms with the coefficients A remain in Eq. (8). If $\Lambda = 0$, only transitions with $\Delta K = \pm 1$ are possible for $\Delta\Lambda = 0$.

The main difficulty in calculating Eq. (8) stands in the evaluation of the radial matrix elements:

$$M(n_1\Lambda_1K_1, n_2\Lambda_2K_2, \ldots, n_f\Lambda_fK_f|E_p) = \left\langle v_f\left|d_N(r)\left(\sum_{v_{N-1}} \frac{|v_{N-1}\rangle\langle v_{N-1}|}{E_0 - E_{N-1} + (N-1)E_p}\right)\right.\right.$$
$$\left.\left.\times d_{N-1}(r)\left(\sum_{v_{N-2}} \frac{|v_{N-2}\rangle\langle v_{N-2}|}{E_0 - E_{N-2} + (N-2)E_p}\right)\cdots d_2(r)\left(\sum_{v_1}\frac{|v_1\rangle\langle v_1|}{E_0 - E_1 + E_p}\right)d_1(r)\right|0\right\rangle . \tag{10}$$

Here $d_i(r)$ ($i = 1, 2, \ldots, N$) is the dipole moment of the ith intermediate electronic transition, i.e., the matrix element (7) in the system of coordinates which rotates with the molecule:

$$d_i(r) = (d)^{n_{i-1}\Lambda_{i-1}}_{n_i\Lambda_i} \quad ;$$

$E_1, E_2, \ldots, E_{N-1}$ are the energies of the successive intermediate states, each of which belongs to a definite electron term with a given value of rotational quantum number K_i.

Each of the $N-1$ summations in Eq. (10) is extended over the complete set of vibrational states of a corresponding virtual electronic state including integration over the continuous spectrum. The matrix elements $\langle v'|d|v\rangle$ are computed over the radial parts $R(r)$ of nuclear wave functions of two electronic states between which the intermediate transition occurs. The function $R_{n\Lambda vk}(r)$ satisfies the equation

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \frac{2m}{\hbar^2}\left(E - \frac{\hbar^2}{2m}\frac{K(K+1)}{r^2} - \mathcal{E}_{n\Lambda}(r)\right)R = 0 , \tag{11}$$

where $\mathcal{E}_{n\Lambda}(r)$ is the potential energy of the $|n\Lambda\rangle$ electronic state.

The matrix element M may be expressed in terms of the Green's functions of the internuclear potentials,

$$g_{n_i\Lambda_iK_i}(r, r'|E) = \sum_{v_i} \frac{|v_i(r)\rangle\langle v_i(r')|}{E - E_i} + \int dE' \frac{|v_{E'}(r)\rangle\langle v_{E'}(r')|}{E - E'} , \tag{12}$$

which satisfy the nonhomogeneous equations

$$\left[\frac{\hbar^2}{2m}\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{K_i(K_i+1)}{r^2}\right) + E - \mathcal{E}_{n_i\Lambda_i}\right] \times g_{n_i\Lambda_iK_i}(r, r'|E) = \frac{\delta(r-r')}{rr'} . \tag{13}$$

With the Green's functions $g_1, g_2, \ldots, g_{N-1}$ for the internuclear potentials of the intermediate-electron terms $|i_1\rangle$, $|i_2\rangle, \ldots,$ i_{N-1}, respectively, Eq. (10) becomes

$$M(n_1\Lambda_1K_1, n_2\Lambda_2K_2, \ldots, n_f\Lambda_fK_f|E_p) = \int_0^\infty R_{qK_f}(r_N)\,d_N(r_N)\,r_N^2\,dr_N$$
$$\times \int_0^\infty d_{N-1}(r_{N-1})\,g_{N-1}[r_{N-1}, r_N|E_0 + (N-1)E_p]\,r_{N-1}^2\,dr_{N-1} \cdots \int_0^\infty d_1(r_1)\,g_1(r_1, r_2|E_0 + E_p)\,R_{vK}(r_1)\,r_1^2\,dr_1, \tag{14}$$

where $R_{vK}(r)$ is the initial-state wave function normalized by the condition.

$$\int_0^\infty R_{vK}^2 r^2\,dr = 1 .$$

III. MULTIPHOTON-EXCITATION CROSS SECTION

Within the framework of time-dependent perturbation theory, the cross section σ, in cm^2, for the absorption of the N photon by a diatomic molecule may be derived in the nonrelativistic-dipole approximation

$$\sigma = (2\pi)^2\left(\frac{I}{I_0}\right)^{N-1} r_e c E_p \left|\sum_{i_1,\ldots,i_{N-1}} \frac{\langle f|\vec{\epsilon}\vec{\mathrm{d}}|i_{N-1}\rangle\cdots\langle i_1|\vec{\epsilon}\vec{\mathrm{d}}|0\rangle}{[E_0 - E_{N-1} + (N-1)E_p]\cdots(E_0 - E_1 + E_p)}\right|^2 g(E_0 + NE_p) . \tag{15}$$

Here r_e is the classical electron radius, $g(E_0 + NE_p)$ is the line shape of the final bound molecular state $|f\rangle$, and $\int g(E)dE = 1$. We assume the final state has a Gaussian shape with the half-width Γ_f:

$$g_f(E) = \frac{1}{\pi^{1/2}\Gamma_f} e^{-(E_f - E)^2/\Gamma_f^2} . \tag{16}$$

Generally speaking, Γ_f depends on the external field intensity; in the energy difference between the molecular levels in the absence of an external field $(E_f - E_0)$, allowance may also be made for the level shift ΔE. [Equation (15) is obtained on the assumption that the half-width Γ of the spectral intensity of the radiation is $\Gamma \ll \Gamma_f$.] The summations over the intermediate states in Eq. (15) are defined by Eq. (8), the factor $(2\pi)^{3/2} q^{-1} (-i)^{K_f} e^{i\delta K_f} \times Y^*_{K_f M}(\Theta, \Phi)$ being neglected, while the radial matrix elements M are calculated by means of Eq. (14) where the bound-state function $R_{vK}(r)$ replaces the continuum wave function for the final state.

IV. POTENTIAL-ENERGY-CURVE MODEL: WAVE FUNCTIONS AND GREEN'S FUNCTIONS

The true potential curve of the ground electronic state of a homopolar diatomic molecule can frequently be satisfactorily described by the Morse potential which has the form

$$V_0(r) = D_0 \left(e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}\right), \tag{17}$$

where D_0 is the quantity shown in Fig. 1, r_0 is the equilibrium internuclear distance, and α is the anharmonicity constant which depends on the half-width Δ of the potential curve $\alpha = 1.76\Delta^{-1}$.

Using the Morse potential as the ground-state potential curve, let us describe the potential curves for the excited electronic states $|i\rangle$ by means of the following expression:

$$V_i(r) = D_i \left(e^{-2\alpha(r-r_0)} - 2t_i e^{-\alpha(r-r_0)}\right) + Q_i\,. \tag{18}$$

When $t_i > 0$, we have the Morse potential

$$V_i(r) = t_i^2 D_i \left(e^{-2\alpha(r-r_i)} - 2e^{-\alpha(r-r_i)}\right) + Q_i\,,$$

where $r_i = r_0 - \alpha^{-1}\ln t_i$. For $t_i < 0$, Eq. (18) gives a good representation of the true repulsive potential curves (see Fig. 1). The radial Schrödinger's equation (11), with Eq. (18) as $V(r)$ and with the new variables $y = 2\beta\, e^{-\alpha(r-r_0)}$ and $W = y^{1/2} rR$, reduces to the standard Whittaker form (we put $K=0$)

$$W'' + \left[-\tfrac{1}{4} + t\beta/y + (\tfrac{1}{4} - \zeta^2)/y^2\right]W = 0\,, \tag{19}$$

where the parameter ζ is $(\alpha\hbar)^{-1}[-2m(E-Q)]^{1/2}$; the subscripts have been omitted for the parameters D, t, and Q and the variable y; $\beta_i = (\alpha\hbar)^{-1} \times (2mD_i)^{1/2}$.

Equation (19) allows two linearly independent solutions. The Whittaker function $M_{t\beta,\zeta}(y)$ is regular for $y \to 0$ and the Whittaker function $W_{t\beta,\zeta}(y)$, the other fundamental solution of Eq. (19), is regular for $y \to \infty$.

The Whittaker functions are defined as

$$M_{t\beta,\zeta}(y) = e^{-y/2} y^{\zeta+1/2}\, \Phi\left(\tfrac{1}{2} - t\beta + \zeta,\, 2\zeta+1,\, y\right) \tag{20}$$

(where Φ is the confluent hypergeometric function[5]) and

$$W_{t\beta,\zeta}(y) = \frac{\Gamma(-2\zeta)}{\Gamma(\frac{1}{2} - \zeta - t\beta)} M_{t\beta,\zeta}(y) + \frac{\Gamma(2\zeta)}{\Gamma(\frac{1}{2} + \zeta - t\beta)} M_{t\beta,-\zeta}(y)\,. \tag{21}$$

The Whittaker functions $M_{t\beta,\zeta}(y)$ are the bound-state eigenfunctions for the attractive potential $(t > 0)$ with the vibrational energy eigenvalues equal to

$$E_v - Q = Dt^2\left[1 - (v + \tfrac{1}{2})(t\beta)^{-1}\right]^2 < 0,$$

where $\zeta - t\beta + \frac{1}{2} = -v$; $v = 0, 1, 2, \ldots$. In this case, the confluent hypergeometric functions in Eq. (20) reduce to the polynomials, and the wave functions

$$rR(r) = y^{-1/2} M_{t\beta,\, t\beta-v-1/2}(y)$$

satisfy the boundary conditions.[6] The normalized wave functions of the discrete spectrum have the form

$$rR_v(r) = \frac{[\alpha(2t\beta - 2v - 1)\,\Gamma(2t\beta - v)]^{1/2}}{(v!)^{1/2}\,\Gamma(2t\beta - 2v)\, y^{1/2}} \times M_{t\beta,\, t\beta-v-1/2}(y)\,. \tag{22}$$

The continuum wave functions $(E - Q > 0)$ in a repulsive $(t < 0)$ or attractive $(t > 0)$ field are represented by the Whittaker functions $W_{t\beta,\, iq/\alpha}(y)$, where $q = [2m(E-Q)]^{1/2}\hbar^{-1}$ is the wave number of the dissociating particles. Such solutions of Eq. (19) are regular at the origin of the coordinates, i.e., for $y \to \infty$. The asymptotic expression for $R_q(r)$ when r is large $(y \to 0)$ may be obtained from Eq. (21),

$$R_q(r) = \frac{(2\pi y)^{-1/2}}{r} \left|\frac{\Gamma(\frac{1}{2} - t\beta + iq/\alpha)}{\Gamma(2iq/\alpha)}\right| W_{t\beta,\, iq/\alpha}(y)$$

$$= \frac{(2\pi y)^{-1/2}}{r}\left[e^{-i\chi} M_{t\beta,\, iq/\alpha}(y) + \text{c.c.}\right], \tag{23}$$

and is of the form

$$R_q(r) \approx (2/\pi)^{1/2}(1/r)\sin(qr + \eta_0)\,,$$

$$\eta_0 = x + \tfrac{1}{2}\pi - qr_0 - (q/\alpha)\ln 2\beta\,, \tag{24}$$

$$\chi = \arg\frac{\Gamma(2iq/\alpha)}{\Gamma(\frac{1}{2} - t\beta + iq/\alpha)}\,.$$

The Green's function for the potential (18) which satisfies Eq. (13) and the necessary boundary conditions may be expressed by means of two fundamental solutions $R^{(a)}$ and $R^{(b)}$ of the homogeneous Eq. (11):

$$g(r,r'|E)=-\frac{2m}{\hbar^2}\left[R^{(a)}(r_<)R^{(b)}(r_>)/r^2\left(R^{(b)}(r)\frac{dR^{(a)}}{dr}-R^{(a)}(r)\frac{dR^{(b)}}{dr}\right)\right]\ .$$

Here $R^{(a)}$ and $R^{(b)}$ are regular for the two singular points a and b of the potential $(a<r<b)$; $r_>$ $(r_<)$ is the larger (smaller) of the two quantities r and r'.[7] Using Eqs. (20) and (21) as the fundamental solutions and calculating the Wronskian gives

$$g(r,r'|E)=-\frac{2m}{\alpha\hbar^2rr'}(yy')^{-1/2}\times\frac{\Gamma(\zeta-t\beta+\frac{1}{2})}{\Gamma(2\zeta+1)}M_{t\beta,\zeta}(y_<)W_{t\beta,\zeta}(y_>)\ , \tag{25}$$

where $y_>(y_<)$ is the larger (smaller) of the quantities y and y'. It is sometimes convenient to use the integral representation of the Green's function (25) ub symmetric coordinates,[8]

$$g(r,r'|E)=-\frac{2m}{\alpha\hbar^2rr'}\int_0^1\frac{s^{-t\beta-1/2}}{1-s}\times\exp\left(-\frac{y+y'}{2}\,\frac{1+s}{1-s}\right)I_{2\zeta}\left(\frac{2(syy')^{1/2}}{1-s}\right)ds$$

$$\mathrm{Re}(\zeta+\tfrac{1}{2}-t\beta)>0\ . \tag{26}$$

V. ELECTRONIC-TRANSITION DIPOLE MOMENTS

Let us describe the electronic-transition dipole moments by the functions

$$d(r)=d_1y^{x_1}+d_2y^{x_2}+\cdots\ . \tag{27}$$

Equation (27) enables a correct description to be given for the transition dipole moments of some homopolar diatomics for large r, as well as in the vicinity of the internuclear equilibrium distance r_0:

$$\begin{aligned}d(r)&=d(r_0)+\frac{d'(r_0)}{\alpha x}(1-e^{-\alpha x(r-r_0)})\\&\simeq d(r_0)+d'(r_0)(r-r_0)\\&\quad-\frac{d'(r_0)\,\alpha x}{2!}(r-r_0)^2+\cdots\ .\end{aligned} \tag{28}$$

To obtain the latter expression, we have put in Eq. (27) $d_{i>2}=0$, $x_1=0$ for the sake of simplicity and have expressed the parameters $d_1>-d_2>0$ in terms of the values of the dipole moment $d(r_0)$ and its derivative $d'(r_0)$ at $r=r_0$. The nonlinear terms in Eq. (28) correspond to the electric anharmonicity of the transition.

VI. METHOD OF EVALUATING RADIAL MATRIX ELEMENTS

The chief difficulty in calculating the $M(i_0, i_1, \ldots, i_{N-1}, i_f\,|\,E_p)$ functions (14) stands in the correct evaluation of the $N-1$ summations. Each of these $N-1$ summations is extended over the complete set of vibrational states v_j (discrete plus continuum) of the given intermediate electron term $|i_j\rangle$.

With Eqs. (22), (23), and (25), the radial matrix elements (14) for the bound-free multiphoton transition can be written (we use the atomic units)

$$\begin{aligned}&M(n_1\Lambda_1K_1,\,n_2\Lambda_2K_2,\,\ldots,\,n_f\Lambda_fK_f)\\&=\frac{(-2m)^{N-1}}{\alpha^{2N-1}}\left(\frac{\alpha}{2\pi}\right)^{1/2}\frac{[(2\beta-2v-1)\Gamma(2\beta-v)]^{1/2}}{(v!)^{1/2}\Gamma(2\beta-2v)}\left|\frac{\Gamma(\frac{1}{2}-t_N\beta+iq/\alpha)}{\Gamma(2iq/\alpha)}\right|\prod_{i=1}^{N-1}\frac{\Gamma(\zeta_i-t_i\beta+\frac{1}{2})}{\Gamma(2\zeta_i+1)}\\&\times\int_0^\infty d_N(y_N)y_N^{-2}W_{t_N\beta,iq/\alpha}(y_N)dy_N\int_0^\infty d_{N-1}(y_{N-1})y_{N-1}^{-2}W_{\beta t_{N-1},\zeta_{N-1}}(y_{N-1},y_N>)\\&\times M_{\beta t_{N-1},\zeta_{N-1}}(y_{N-1},y_N<)dy_{N-1}\cdots\int_0^\infty d_1(y_1)y_1^{-2}M_{\beta t_1,\zeta_1}(y_2,y_1<)W_{\beta t_1,\zeta_1}(y_2,y_1>)M_{\beta,\beta-v-1/2}(y_1)dy_1\ .\end{aligned} \tag{29}$$

Here $d_1(y_1)$, $d_2(y_2)$, $\ldots$, $d_N(y_N)$ are the first, second, $\ldots$, Nth intermediate electronic-transition dipole moments; the quantities $\zeta_i=\alpha^{-1}h^{-1}[-2m\times(E_0-Q_i+iE_p)]^{1/2}$ determine dependence of the Green's functions on the energy; the parameters t_i and Q_i determine the internuclear potentials (18) for the $N-1$ intermediate and the final electronic states, $t_0=1$. For the sake of simplicity we assume that $\beta_1=\beta_2=\cdots=\beta$. The Whittaker functions $M(y_i, y_{i+1}^{<})$ and $W(y_i, y_{i+1}^{>})$ in Eq. (29) are the functions of the smaller and of the larger, respectively, of the two quantities y_i and y_{i+1}; v is the vibrational quantum number of the initial state. Expression (29) may be represented as the sum of integrals of the Whittaker functions of the form

$$\int_0^\infty\frac{d_N(y_N)}{y_N^2}W_{t_N\beta,iq/\alpha}(y_N)M_{t_N\beta,\zeta_{N-1}}(y_N)dy_N$$

$$\times \int_{y_N}^{\infty} \frac{d_{N-1}(y_{N-1})}{y_{N-1}^2} W_{t_{N-1}\beta,\,\zeta_{N-1}}(y_{N-1})$$

$$\times M_{t_{N-2}\beta,\,\zeta_{N-2}}(y_{N-1})\,dy_{N-1} \cdots$$

$$\times \int_{y_2}^{\infty} W_{\beta t_1,\,\zeta_1}(y_1) \frac{d_1(y_1)}{y_1^2} M_{\beta,\,\beta-v-1/2}(y_1)\,dy_1 \,. \quad (30)$$

Since each inner integral in (30) has a single variable limit, integration with a constant interval makes (30) actually equivalent to a simple integral. The Whittaker functions in Eq. (30) may be calculated using the expansions into convergent power series and known integral representations.[5]

Without going into the problems of numerical integration of the expressions (30) it may be noted that results can, in the case of one- and two-photon transitions, be expressed in an analytic form. This relates in the first instance to the one-photon transitions, which play an important part in diatomic molecular spectroscopy.

VII. ONE-PHOTON VIBRONIC TRANSITIONS

Let us first consider a one-photon bound-bound transition which occurs between two vibrational levels v and v' belonging to discrete vibrational spectra of the two electronic states $|0\rangle$ and $|1\rangle$, respectively. A transition that involves both electronic and vibrational transitions is referred to as a vibronic transition, and the combining terms are referred to as vibronic terms. Using expressions (22) for the nuclear wave functions of the initial ($t=1$) and the final ($t>0$) vibronic terms and integrating,[9] we get (for $\beta+t\beta+x-v-v'>1$)

$$I(dy^x)=\int_0^{\infty} R_v^{(0)}(r)dy^x R_{v'}^{(1)}(r)r^2dr=(-1)^{v'}d\left(\frac{(2\beta-2v-1)(2t\beta-2v'-1)\Gamma(2\beta-v)}{v!\,v'!\,\Gamma(2t\beta-v')}\right)^{1/2}$$

$$\times\sum_{m=0}^{v}\frac{(-v)_m\Gamma(x-1+\beta-v+t\beta-v'+m)\Gamma(x+\beta-v-t\beta+v'+m)}{m!\,\Gamma(2\beta-2v+m)\Gamma(x+\beta-v-t_\beta+m)}\,. \quad (31)$$

Using the asymptotic expansion (Stirling series) for the Γ functions which appear in Eq. (31) (this approximation ensures high precision for $2\beta-2v\gg1$, $\beta+t\beta-v-v'\gg1$), the matrix element I can be written

$$I=(-1)^{v'}\frac{d}{(v!\,v'!)^{1/2}}[2\beta-2v-1)(2\beta'-2v'-1)]^{1/2}e^{(v'-v)/2-x+1}(\beta-\beta'+x-v)_{v'}\frac{(2\beta-v)^{\beta-v/2-1/4}}{(2\beta'-v')^{\beta'-v'/2-1/4}}$$

$$\times(2\beta-2v)^{-2\beta+2v+1/2}(\beta+\beta'+x-v-v'-1)^{\beta+\beta'+x-v-v'-3/2}\sum_{m=0}^{v}\frac{(-v)_m(\beta+\beta'+x-v-v'-1)_m(\beta+x-\beta'-v-v')_m}{m!(2\beta-2v)_m(\beta-\beta'+x-v)_m}\,, \quad (31')$$

where $\beta'=t\beta$, $(a)_m=a(a+1)\ldots(a+m-1)$. When $t=1$, Eq. (31) describes the vibrational transitions which take place without change in the electronic state. In this case, for $x=0$, we have $I(d)=d\delta(v,v')$ owing to the orthogonality of the vibrational wave functions belonging to one and the same electronic state.

The linear approximation for the dependence of the transition dipole moment on the internuclear distance can be obtained from

$$d(r)=d_0+dy^x\,, \quad (32)$$

when the coefficients d_0 and d behave as $d_0=d(r_0)+\alpha^{-1}x^{-1}d'(r_0)$ and $d=-d'(r_0)\alpha^{-1}x^{-1}(2\beta)^{-x}$ as $x\to0$, giving rise to fixed values of $d(r_0)$ and $d'(r_0)$ in Eq. (32):

$$d(r)=d(r_0)+\frac{d'(r_0)}{\alpha x}-\alpha^{-1}x^{-1}d'(r_0)\left(\frac{y}{2\beta}\right)^x$$

$$=d(r_0)+d'(r_0)(r-r_0)-\frac{\alpha x d'(r_0)}{2!}(r-r_0)^2+\cdots\,. \quad (33)$$

Owing to the orthogonality of the wave functions at $t=1$, the integral (31) as the function of the first term in Eq. (32) (which increases infinitely as $x\to0$) is equal to zero $I(d_0)\equiv0$.

To calculate (31) as the function of the second term in Eq. (32) we have the known relationship

$$\lim_{x\to0}[x\Gamma(x-v+m)]=\frac{(-1)^{v-m}}{(v-m)!}=\frac{(-1)^v(-v)_m}{v!}$$

and the Gaussian summation theorem for hypergeometric series $F_1(a,b,c;1)$.[10] Finally, we obtain the expression (we assume that $v'>v$)

$$I(r)=\int_0^\infty R_v^{(0)}(r)R_{v'}^{(0)}(r)\,r^3\,dr=\frac{(-1)^{v+v'}\quad[(v')!\,(2\beta-2v-1)(2\beta-2v'-1)\,\Gamma(2\beta-v')]^{1/2}}{\alpha(v-v')(2\beta-v-v'-1)[v!\,\Gamma(2\beta-v)]^{1/2}}\quad, \tag{34}$$

which makes it possible to evaluate, in Eq. (31), the effect of the electric anharmonicity on the probability of the vibrational transitions.

Let us now turn to the analysis of one-photon bound-free transitions (photodissociation). Let us write the initial wave function, defined by Eq. (22), in the form

$$R_v^{(0)}(r)=\frac{(\alpha v!)^{1/2}(2\beta-2v-1)^{1/2}}{r[\Gamma(2\beta-v)]^{1/2}}\times e^{-y/2}y^{\beta-v-1/2}L_v^{2\beta-2v-1}(y)\,, \tag{35}$$

where

$$L_v^{2\beta-2v-1}(y)=\frac{(2\beta-2v)v}{v!}\,\Phi(-v,2\beta-2v,y)=\sum_{l=0}^{v}a_l^{(v)}y^{v-l} \tag{36}$$

are the Laguerre polynomials. Using Eq. (23) for the continuum wave function of the final vibronic term $|1\rangle$ and integrating,[11] we get, after some transformations,

$$I(dy^x)=\int_0^\infty R_v^{(0)}\,dy^x R_q^{(1)}\,r^2dr=\frac{d(qv!)^{1/2}(2\beta-2v-1)^{1/2}\sinh^{1/2}(2\pi q/\alpha)|\Gamma(\frac{1}{2}-t\beta+iq/\alpha)|}{\alpha\pi[\Gamma(2\beta-v)]^{1/2}}\times\sum_{l=0}^{v}a_l^{(v)}\,\frac{|\Gamma(iq/\alpha+\beta+x-\frac{1}{2}-l)|^2}{\Gamma(\beta+x-t\beta-l)}\quad. \tag{37}$$

Excluding vibronic transitions from high vibrational levels in the vicinity of the photodissociation threshold and some transitions to bound electronic states ($t>0$), the arguments of the Γ functions in Eq. (37) are large. With the corresponding asymptotic expressions, Eq. (37) can be written

$$I(dy^x)=\frac{dq^{1/2}}{\alpha}\left(\frac{2}{\pi}\right)^{1/4}(2\beta-2v-1)^{1/2}\,\frac{\exp(\pi q/\alpha+\frac{1}{2}-x-\frac{1}{2}v)}{(2\beta-v)^{\beta-v/2-1/4}}\left[\left(\frac{q}{\alpha}\right)^2+(\tfrac{1}{2}-t\beta)^2\right]^{-t\beta/2}\times\exp\left(-\frac{q}{\alpha}\tan^{-1}\frac{q}{\alpha(\frac{1}{2}-t\beta)}\right)\sum_{l=0}^{v}a_l^{(v)}\,\frac{[(q/\alpha)^2+(\beta+x-\frac{1}{2}-l)^2]^{\beta+x-1-l}}{(\beta+x-t\beta-l)^{\beta+x-t\beta-1/2-l}}\,\exp\left(l-\frac{2q}{\alpha}\tan^{-1}\frac{q}{\alpha(\beta+x-\frac{1}{2}-l)}\right)\,. \tag{38}$$

To reveal analytically the dependence of the matrix elements of one-photon vibronic transitions on the electric anharmonicity of the transition dipole moment, let us use in Eq. (37) the following approximation:

$$\frac{|\Gamma(iq/\alpha+\beta+x-\frac{1}{2}-l)|^2}{\Gamma(\beta-t\beta+x-l)}=\left(\frac{(q/\alpha)^2+(\beta-\frac{1}{2}-l)^2}{\beta-t\beta-l}\right)^x\times\frac{|\Gamma(iq/\alpha+\beta-\frac{1}{2}-l)|^2}{\Gamma(\beta-l-t\beta)}\quad, \tag{39}$$

obtained with the help of the asymptotic expression[12]

$$\frac{\Gamma(z+x)}{\Gamma(z)}=z^x\left(1+\frac{x(x-1)}{2z}+O(z^2)\right)\,.$$

Thus, for $v=0$, using Eqs. (33), (37), and (39), we get

$$I\left[d(r_0)+\frac{d'(r_0)}{\alpha x}-\frac{d'(r_0)}{\alpha x}\left(\frac{y}{2\beta}\right)^x\right]=\left[d(r_0)+\frac{d'(r_0)}{\alpha x}-\frac{d'(r_0)}{\alpha x(2\beta)^x}\left(\frac{(q/\alpha)^2+(\beta-\frac{1}{2})^2}{\beta(1-t)}\right)^x\right]I(1)\,, \tag{40}$$

where $I(1)$ is the function (37) for $x=0$, $d=1$. Expanding the expression on the right-hand side in inner parentheses in Eq. (40) in a power series of the small parameter x (usually $x<0.1$), we have

$$I(d_0+dy^x)=\left[d(r_0)-\frac{d'(r_0)}{\alpha}\times\left(\ln a+\frac{x\ln^2 a}{2!}+\frac{x^2\ln^3 a}{3!}+\cdots\right)\right]I(1)\,, \tag{41}$$

where $a=[(q/\alpha)^2+(\beta-\frac{1}{2})^2]\,[2\beta(\beta-t\beta]^{-1}$. In the linear approximation we have $d(r)=d(r_0)+d'(r_0)\,(r-r_0)$

and

$$I(d(r_0)+d'(r_0)(r-r_0))$$

$$=\left(d(r_0)-\frac{d'(r_0)}{\alpha}\ln\frac{(q/\alpha)^2+(\beta-\frac{1}{2})^2}{2\beta^2(1-t)}\right)I(1). \tag{42}$$

Thus, the term in Eq. (41), which is proportional to x, describes, as a first approximation, the effect of the electric anharmonicity of the transition dipole moment.

The expressions obtained in this section may be used to evaluate the one-photon transition probability in real homopolar diatomics. As an illustration we shall consider the photodissociation of H_2^+ from the $v=0$ vibrational level. Furthermore, this example allows us to compare the cross sections calculated from Eq. (41) with the cross sections calculated in Ref. 13 using accurate wave functions.

Using general Eqs. (2) and (8) in the case $N=1$, summing over initial M degeneracy, and integrating over the solid angle, we have for the one-photon dissociation cross section,[13]

$$\sigma_v=\left(\frac{2m}{m_{H_2^+}}\right)^{1/2}4.08\times10^{-17}\frac{E_p}{(E_v+E_p)^{1/2}}\,I^2(d(r)). \tag{43}$$

Here E_v is the eigenenergy of the vibrational level from which the dissociation occurs, $m_{H_2^+}$ is the reduced mass of H_2^+, and the radial matrix element I is defined in Eq. (37); σ_v is in cm^2, all other terms are in atomic units.

Relevant potential curves (18) for H_2^+ are shown in Fig. 1 as well as the accurate curves.[13] Transitions considered are from the $v=0$ level of H_2^+ in the $1s\sigma_g$ electronic state to various parts of the vibrational continuum of the $2p\sigma_u$ state. The $1s\sigma_g \rightarrow 2p\sigma_u$ transition dipole moment calculated in Ref. 14 using accurate wave functions of H_2^+ is also shown in Fig. 1 as well as the function (32) with $d(r_0)=1.07$, $d'(r_0)=0.396$, and $x=-0.055$. The matrix element I is calculated from Eq. (41) and $I(1)$ from the asymptotic expression (38). The contribution of the terms describing the electric anharmonicity proved in this case to be negligible.

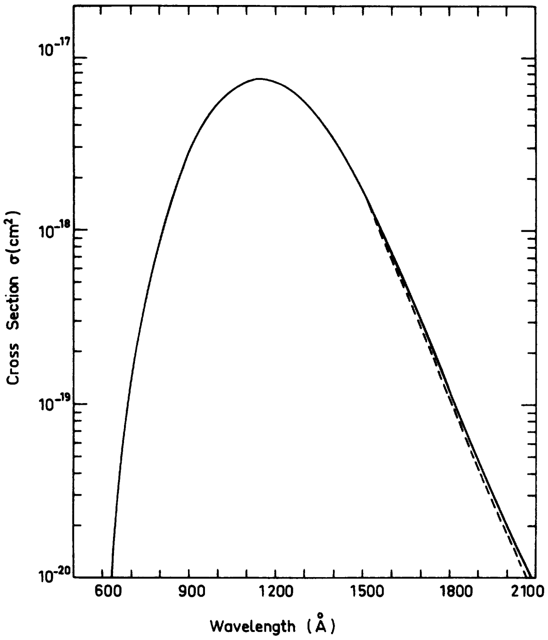

FIG. 2. Photodissociation cross section of H_2^+ from $v=0$ vibrational level. The solid curve shows the cross section as calculated in Ref. 13 using accurate wave functions. The dashed curve shows the results, calculated from the analytic expression (42) using the model of $V_0(r)$, $V_1(r)$, and $d(r)$ presented in Fig. 1.

The solid curve in Fig. 2 shows the cross section as the function of wavelength for photodissociation of H_2^+ from the $v=0$ vibrational level as calculated in Ref. 13 using accurate wave functions. The dashed curve shows the results calculated from Eq. (42). It is evident from Fig. 2 that in this case the model of internuclear potentials (18) and that of transition dipole moments (32) give results very close to the true values.

VIII. TWO-PHOTON TRANSITIONS

Using the integral representation (26) for the Green's functions of the intermediate states, the radial matrix element (29) for any two-photon transition can be represented in an analytic form. Thus, in the case of bound-bound transitions, we find, after integrating over y_1,[15] the following expression for the radial matrix element (14) calculated for the value $N=2$:

$$M(v,v'\,|\,E_p)=\sum_{i,j}^{1,2}d_i\,d_j\,M^{x_i,x_j},$$

$$M^{x_i,x_j}=\int_0^\infty\int R_v^{(0)}(r)\,y_1^{x_i}\,r_1^2dr_1\,g_1(r_1,r_2\,|\,E_0+E_p)\,y_2^{x_j}\,R_{v'}^{(f)}(r_2)\,r_2^2dr_2$$

$$=-\frac{2m}{\alpha^2}\left(\frac{v!}{v'!}\right)^{1/2}\frac{(2\beta-2v-1)^{1/2}}{\Gamma(2t'\beta-2v')\,\Gamma(2\xi+1)}\left(\frac{(2t'_\beta-2v'-1)\,\Gamma(2t'\beta-v')}{\Gamma(2\beta-v)}\right)^{1/2}\sum_{l=0}^{v}a_l^{(v)}$$

$$\times \Gamma(\beta - \tfrac{1}{2} + x_i + \zeta - l) \int_0^\infty dy_2\, y_2^{x_j - 2} M_{t'\beta,\, t'\beta - v' - 1/2}(y_2) \int_0^1 ds\, \frac{(1-s)^{\beta - 1 - l + x_i}}{s^{t_i \beta + 1}}\, e^{-y_2/2(1-s)}\, M_{-\beta+1-x_i+l,\, \xi}\left(\frac{sy_2}{1-s}\right) . \tag{44}$$

Integrating over y_2,[16] and using the standard integral representation for the B function, we get

$$M^{x_i, x_j} = -\frac{2m(2\beta - 2v - 1)^{1/2}}{\alpha^2} \left(\frac{v!\,(2t'\beta - 2v' - 1)\,\Gamma(2t'\beta - v')}{v'!\ \Gamma(2\beta - v)}\right)^{1/2}$$

$$\times \sum_{l=0}^{v} a_l^{(v)} \sum_{m=0}^{v'} \sum_{n=0}^{\infty} \left(\frac{(-v')_m\, \Gamma(a_1 + m + n)\, \Gamma(a_2 + m)\, \Gamma(a_3 + n)\, \Gamma(a_4 + n)}{m!\, n!\ \Gamma(b_1 + m + n)\, \Gamma(b_2 + m)\, \Gamma(b_3 + n)}\right) , \tag{45}$$

where

$$a_1 = t'\beta + \zeta + x_j - v' - \tfrac{1}{2} ,$$

$$a_2 = \beta(1 + t') + x_i + x_j - v' - 1 - l ,$$

$$a_3 = \beta + \zeta + x_i - l - \tfrac{1}{2} ,$$

$$a_4 = \zeta - t_i\beta + \tfrac{1}{2} ;$$

$$b_1 = a_2 + a_4 ,\ b_2 = 2t'\beta - 2v' ,\ b_3 = 2\zeta + 1 .$$

Here v and v' are the vibrational quantum numbers of the initial and final vibronic states, respectively; β is a constant related to the parameters of the Morse potential (17) of the ground state, $\beta = (2mD)^{1/2}(\alpha h)^{-1}$. The parameters t_i and t' determine the potentials (18) for the intermediate and the final electronic states, respectively, $\zeta = \beta \times [-(E_0 - Q_i + E_p)/D]^{1/2}$ determines the Green's-function energy dependence.

The $(v+1)$ generalized hypergeometric series ${}_3F_2(a, b, c; d, e; 1)$, which appear in Eq. (45) for the fixed values $m = 0, 1, \ldots, v'$, converge very slowly. However, the numerical operating of these series is straightforward, since the terms S_n in the expansion

$${}_3F_2(a, b, c; d, e; 1) = \sum_{n=0}^{\infty} S_n$$

are related by a simple recursion relation $S_{n+1} = B(n) S_n$.[17]

Note, finally, that in the case of two-photon bound-free transitions the radial matrix elements (14) can also be reduced to the form analogous to Eq. (45).

IX. CONCLUSION

In performing the calculations described in Secs. I–VIII our purpose was to demonstrate that using the Born–Oppenheimer approximation and explicit expressions for the Green's functions of empirical internuclear potentials, which give a good representation of true curves, one gets a constructive approach to the consideration of multiphoton transitions in diatomic molecules. The main difficulty of the problem stems from the complexity of the molecular structure: Whereas the spectra of atoms are due to electronic transitions, the molecular spectra can be related to electronic, vibrational, and rotational transitions. Furthermore, these modes are not independent of each other and the complexity of the spectra may be compounded by the possibility of interaction between them. Dynamic-coupling phenomena–autoionization and predissociation of a molecule–play an important part in some multiphoton transitions in H_2.[18] On the other hand, the use of separability of wave functions and then of the Green's functions of internuclear potentials obtained in closed form do give the possibility of treating the multiphoton transitions in the molecule. After the selection rules for rotational and electronic quantum numbers have been established, the problem is reduced essentially to that of calculating radial matrix elements which contain the Green's function of internuclear potentials of corresponding intermediate electronic states. There are reasons for hoping that further development of methods of experimental[19,20] and theoretical research into multiphoton transitions in molecules will play an important part in both nonlinear molecular spectroscopy and more extensive investigations of the interaction of laser radiation with matter.

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[3] The selection rules for the other quantum numbers which determine the electron state of the molecule may also be mentioned. If both the terms are Σ terms ($\Lambda=0$) the component d_ξ has nonzero matrix elements only for the transitions $\Sigma^+ \rightarrow \Sigma^+$ and $\Sigma^- \rightarrow \Sigma^-$. If the molecule consists of similar atoms, the matrix elements are nonzero only for transitions between states of different parity.

[4] See Ref. 2, Eqs. (87.4) and (87.1).

[5] H. Buchholz, *The Confluent Hypergeometric Function* (Springer, Berlin, 1969).

[6] As in the case of the Morse potential, the boundary conditions are defined in the singular points of the potential (18), i.e., for $y=0$ and $y=\infty$, corresponding to $r=\infty$ and $r=-\infty$. This approximation does not give rise to any substantial errors, since the functions $rR(r)$ will be extremely small at $r=0$.

[7] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953), Vol. 1, p. 524.

[8] See Ref. 5, p. 86, Eq. (5c) and make the change of variables $s=(\cosh v-1)/(\cosh v+1)$. By an analytic continuation argument, we find that the integral representation for the product of the two functions $M_{t\beta,\zeta}(y)$ and $W_{t\beta,\zeta}(y)$ holds without the restriction $\mathrm{Re}(\zeta - t\beta+\frac{1}{2})>0$ [L. Hostler, J. Math. Phys. 5, 591 (1964)]. By going over from the real to the contour integral (which begins at $s=1$, circles the point $s=0$ in the positive sense and then returns to $s=1$) we must introduce on the right-hand side in Eq. (26) the factor $\exp[\pi i(t\beta-\zeta+\frac{1}{2})]/2i\sin[\pi(\zeta-t\beta-\frac{1}{2}]$.

[9] A. Erdelyi, W. Magnus, F. Oberhettinger, and F. Tricomi, *Tables of Integral Transform* (McGraw-Hill, New York, 1954), Vol. 1.

[10] A. Erdelyi, W. Magnus, F. Oberhettinger, and F. Tricomi, *Higher Transcendental Functions* (McGraw-Hill, New York, 1953), Vol. 1.

[11] To integrate we made use of Eq. (16) given in Ref. 9, p. 216 and assume that $\beta - v + x > \frac{1}{2}$.

[12] See Ref. 10, p. 47, Eq. (4).

[13] G. H. Dunn, Phys. Rev. **172,** 1 (1968).

[14] D. R. Bates, J. Chem. Phys. **19,** 1122 (1951).

[15] We use in (14) Eqs. (35) and (22) for the radial wave functions of the initial and final states, respectively, and Eq. (26) for the Green's function of the intermediate term. For integration over y_1 see Ref. 9, p. 197, Eq. (20). We assume that $\beta - v + \zeta + x_i > \frac{1}{2}$.

[16] See Ref. 9, p. 216, Eq. (14). We assume that $t'\beta - v' + \zeta + x_j > \frac{1}{2}$ and $t'\beta - v' + \beta - v + x_i + x_j > 1$.

[17] Equation (45) has been used to calculate the two-photon excitation of H_2^+. See M. Trahin and I. I. Tugov (unpublished).

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Perturbation Theory in Closed Form for Heteronuclear Diatomic Molecules

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Within the framework of the Born–Oppenheimer approximation questions are considered involving application of time-dependent perturbation theory to diatomic heteronuclear molecules. A potential-energy model of the form $V_i(r)=A_i/(r-r_i)^2-B_i/(r-r_i)+Q_i$ is proposed which gives a good representation of the true curves of the ground and excited states of a molecule. The relation $\omega_e x_e = 6D^2/m = 3\omega_e^{4/3}/2m^{1/3}$ has been obtained between the dissociation energies into free ions D, vibrational frequencies ω_e, and vibrational anharmonicity parameters $\omega_e x_e$ of the ground state of polar molecules. Analytical expressions are derived for vibration-rotation spectra, wave functions, and radial matrix elements considered in the first-order perturbation theory. An explicit expression obtained for the Green's function of the model enables a closed form to be given for matrix elements appearing in the higher-order perturbation theory involved in calculation of multiphoton molecular transitions.

I. INTRODUCTION

Perturbation theory is one of the most promising approaches to molecular quantum mechanics and particularly to multiphoton processes in nonlinear optical phenomena. Application of time-dependent perturbation theory ordinarily leads to multiple infinite summations of matrix elements over discrete energy states and to integration over continuum spectrum of the unperturbed Hamiltonian. Unfortunately, in most molecular problems, it is difficult to construct a satisfactory unperturbed Hamiltonian for which the complete set of eigenfunctions and eigenvalues is known. Using, as a first-order approximation, the usual separability of the wave functions (Born–Oppenheimer), the application of the perturbation theory to molecular problems may be considerably simplified.