MULTIPHOTON DETACHMENT OF NEGATIVE IONS

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A theory is presented to describe multiphoton detachment of negative ions by intense laser beams. The detachment rate is expressed in terms of the single-photon detachment rate. Numerical results are presented for detachment of electrons from O^- and O_2^-. Critical comments are given concerning some theories of multiphoton ionization.

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I INTRODUCTION

The intense electromagnetic fields obtainable in laser beams can induce multiphoton transitions in atoms and molecules with significant probabilities. A variety of such transitions have been observed.* Also, a number of theoretical studies of these processes have been published. The simplest of these are essentially dimensional analyses[3] and are very crude, but do provide useful scaling relations in the weak field limit.

The most straightforward of the calculations of multiphoton transitions use perturbation theory.[4] These calculations are, unfortunately, of great numerical complexity and are consequently ordinarily carried out with such gross approximations that the results are probably not much more accurate than are those of the above-mentioned dimensional analyses. The perturbation calculations, of course, fail to describe transitions in very strong fields.

A somewhat intuitive and partly phenomenological calculation by Keld"sh[5] takes account of distortion of the atom or molecule by the intense fields and also of transitions taking place through a nearly resonant intermediate state. Keldysh's theory is not restricted to the

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* Several reviews of multiphoton processes are available in the literature.[1†] See also R. A. Fox et al.[2]

† References are listed at the end of the report.

weak field limit, as is perturbation theory, and at the same time provides rather simple expressions for the transition rates.

A technique developed from first principles and not restricted to perturbation theory has been published by Reiss.[6]

The specific process studied in this report is the detachment of an electron from a negative ion by multiphoton absorption. It will be assumed that the photon energy $\hbar\omega$ is significantly less than the detachment potential I. Our method is not applicable for evaluation of ionization of neutral atoms or molecules unless the Coulomb potential in the final state is screened at distances less than $(\hbar\omega/e^2)$. Study of the failure of our theory for ionization processes demonstrates what appear to be significant inaccuracies in the theories of both Keldysh and Reiss.

Certain approximations will be made. These are:

(1) The electromagnetic field of the laser is treated classically and is assumed to vary sinusoidally with the frequency ω. This implies that the beam is intense enough that quantum fluctuations of the $\vec{E}$ and $\vec{B}$ fields are negligible and also that the beam coherence time is long compared with that for the transition to occur.

(2) It is assumed that only electric dipole transitions need be considered, that the photon wavelength is very large compared with atomic dimensions, and that relativistic corrections for electronic motion may be neglected.

(3) We shall assume that only a single electron orbital is involved in the transition. That is, we shall treat the problem as though it were the case of a single electron moving in a specified binding potential. We thus avoid the complexity of many-body interactions.

II FORMULATION

Let $h \equiv h(\vec{p},\vec{x})$ represent the Hamiltonian of the atom (or molecule). Here we suppress the explicit dependence on all coordinates except the momentum $\vec{p}$ and space coordinate $\vec{x}$ of the "active" electron. In the presence of the electromagnetic field the full Hamiltonian is

$$H \equiv h(\vec{p} - \vec{a}, \vec{x}) \tag{1}$$

where

$$\vec{a} \equiv \frac{e}{c}\vec{A} \tag{2}$$

with $\vec{A}$ the vector potential of the electromagnetic field. We shall treat the vector potential as classical, writing it in the form

$$\vec{a} = \left(e\frac{\vec{E}_o}{\omega}\right)\cos(\omega t + \phi_o) \tag{3}$$

where ω is the angular frequency of the field and ϕ_o is a constant. We note that

$$-\dot{\vec{a}} = e\vec{E} = e\vec{E}_o \sin(\omega t + \phi_o)$$

$$e\dot{\vec{E}} = \omega^2\vec{a} \quad . \tag{4}$$

Here $\vec{E}$ is the electric-field intensity.

The Hamiltonian, Eq. (1), may be written as

$$H = H_o + \Delta \tag{5}$$

with

$$\Delta \equiv \vec{p} \cdot \vec{a}/m$$

$$H_o \equiv h + \frac{a^2}{2m} \quad . \tag{6}$$

The quantity H_o represents the "unperturbed" Hamiltonian, and Δ the part that leads to transitions. It would evidently not be sensible to treat the term $a^2/2m$ as an interaction, since this C-number commutes with the electron variables.

The initial state of the ion (or atom) with the active electron bound to it is ϕ_a, where

$$h \phi_a = W_a \phi_a \quad . \tag{7}$$

The solution of the time-dependent Schrödinger equation

$$H_o \phi = i \dot{\phi} \tag{8}$$

corresponding to the initial state, is then

$$\phi(t) = \phi_a e^{-iW_a t} e^{-i\gamma(t)} \tag{9}$$

where

$$\gamma(t) \equiv \int_o^t a(t')^2/2m dt' \quad . \tag{10}$$

The final state, when the electron is out of range of the potential of the residual ion (or atom), is ϕ^f. This satisfies the Schrödinger equation

$$[(\vec{p} - \vec{a})^2/2m]\,\phi^f = i\dot{\phi}^f \quad , \tag{11}$$

or

$$\phi^f = (2\pi)^{-3/2}\, e^{i\vec{k}\cdot\vec{x}}\, e^{-i\gamma_k(t)} \tag{12}$$

where

$$\gamma_k(t) = \int_0^t \left\{[\vec{k} - \vec{a}(t')]^2/2m\right\} dt' \quad . \tag{13}$$

The complete process is described by the wave function $\psi(t)$ that satisfies the full Schrödinger equation

$$H\psi = i\dot{\psi} \tag{14}$$

with the boundary condition that

$$\lim_{t\to+\infty} \psi(t) = \phi^f(t) \quad . \tag{15}$$

If we imagine the electromagnetic field to be turned on very slowly in the remote past and off very slowly in the remote future, the S-matrix for the transition is*

$$S = \lim_{t\to+\infty} \left(\psi(t),\, \phi(t)\right) \quad . \tag{16}$$

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* See, for example, M. L. Goldberger and K. M. Watson.[7] Note that the outgoing-plane-wave boundary condition is used in Eq. (16).

Following standard wave-packet arguments, we have

$$S = -i \int_{-\infty}^{\infty} dt \left[-i \frac{\partial}{\partial t} (\psi, \phi)\right]$$

$$= -i \int_{-\infty}^{\infty} dt \left[(i\dot{\psi}, \phi) - (\psi, i\dot{\phi})\right]$$

$$= -i \int_{-\infty}^{\infty} dt \left(\psi(t), \Delta(t)\phi(t)\right) \quad . \tag{17}$$

A perhaps more useful form for the S-matrix is obtained on making the gauge transformation

$$\psi = e^{i\vec{x}\cdot\vec{a}} \underline{\psi} \quad . \tag{18}$$

This transforms Eq. (14) into the form

$$(h + F)\underline{\psi} = i\dot{\underline{\psi}} \tag{19}$$

where

$$F(t) = -e\vec{x} \cdot \vec{E}(t) \quad . \tag{20}$$

The S-matrix in this representation is

$$S = -i \int_{-\infty}^{\infty} dt \left(\underline{\psi}(t), F(t)\underline{\phi}(t)\right) \quad . \tag{21}$$

Here

$$\underline{\phi}(t) = \varphi_a e^{-iW_a t} \quad . \tag{22}$$

The total rate of ionization is obtained from the expression

$$R = \sum_{\vec{k}} \frac{1}{T} \left| \int_{-\frac{T}{2}}^{\frac{T}{2}} dt(\psi, \Delta\Phi) \right|^2 \qquad (23)$$

or

$$R = \sum_{\vec{k}} \frac{1}{T} \left| \int_{-\frac{T}{2}}^{\frac{T}{2}} dt(\Psi, F\Phi) \right|^2 . \qquad (24)$$

Here T is some long time interval, chosen large enough that R is independent of T.

The expressions (21) and (24) were used by Keldysh[6] in his discussion of multiphoton ionization.

III THE QUASISTATIC APPROXIMATION

In this section we discuss a low-frequency approximation, assuming that

$$\hbar\omega \ll I_a \equiv -W_a \tag{25}$$

The condition (25) was assumed also by Reiss[6] and by Keldysh.[5]

The limit (25) suggests that we begin with solutions to the eigenvalue equation

$$H\chi^{\pm}_{\vec{k}} = W_{\vec{k}}\chi^{\pm}_{\vec{k}} \tag{26}$$

where

$$\chi^{\pm}_{\vec{k}} = (2\pi)^{-3/2} e^{i\vec{k}\cdot\vec{x}} \quad , \qquad \lim_{x\to\infty} \tag{27}$$

consistent with Eq. (15). The transformation

$$\chi^{\pm}_{\vec{k}} = e^{i\vec{x}\cdot\vec{a}} \phi^{\pm}_{\vec{k}} \tag{28}$$

converts Eq. (26) into the form

$$h\phi^{\pm}_{\vec{K}} = W_{\vec{k}}\,\phi^{\pm}_{\vec{K}} \quad .$$

The boundary condition (27) leads us to conclude that

$$\vec{K} = \vec{k} - \vec{a}$$

$$W_{\vec{k}} = K^2/2m \equiv \epsilon_k \tag{29}$$

so the $\phi^{\pm}_{\vec{K}}$ satisfy the Lippmann-Schwinger equation

$$h\phi^{\pm}_{\vec{K}} = \epsilon_K \phi^{\pm}_{\vec{K}} \quad . \tag{30}$$

If $\vec{a}$ can be treated as slowly varying, one might then expect that

$$\psi \cong \chi^{-}_{\vec{k}} \; e^{-i\gamma_k(t)} \tag{31}$$

$$\psi \cong \phi_{\vec{K}} \; e^{-i\gamma_k(t)} \tag{32}$$

would provide approximate solutions to the time-dependent Schrödinger equation. The conditions under which Eqs. (31) and (32) are valid approximations will be studied in the next section.

If, for the moment, we assume that Eqs. (31) and (32) are valid, the expression (21) takes a rather simple form. We have

$$S = -i \int_{-\infty}^{\infty} dt e^{i\left[I_a t + \gamma_k(t)\right]} \left(\phi^{-}_{\vec{K}}, ex\phi_a\right) \cdot \vec{E}_o \sin(\omega t + \phi_o) \quad . \tag{33}$$

Now

$$\vec{d} \equiv \left(\bar{\phi}_{\vec{K}} \quad , \quad e\vec{x}\phi_a \right)$$

is just the dipole matrix element for the single-photon photoelectric process. Thus, knowledge of this matrix element will enable one to evaluate the multiphoton transition rate when Eq. (32) is valid.

For evaluation of the expression (33) the Fourier series expansion of Keldysh is convenient. First we define

$$S_o \equiv -\frac{\omega}{2\pi} \int_0^{\frac{2\pi}{\omega}} dt \, \sin(\omega t + \phi_o) \exp\left\{ i[I_a r + \gamma_k(t)] \right\}$$

$$\times \left(\bar{\phi}_{\vec{K}} \quad , \quad e\vec{x}\phi_a \right) \cdot \vec{E}_o \tag{34}$$

to obtain

$$S = +2\pi i \sum_{\nu=-\infty}^{\infty} \delta\left(I_a + \epsilon_k + \frac{e^2 E_o^2}{4m\omega^2} - \nu \hbar \omega \right) S_o \quad . \tag{35}$$

Equations (34) and (35) were used by Keldysh, but with $\bar{\phi}_{\vec{K}}$ replaced by a plane wave:

$$\bar{\phi}_K \approx (2\pi)^{-3/2} \, e^{i\vec{K}\cdot\vec{x}} \quad . \tag{36}$$

IV STUDY OF THE QUASISTATIC APPROXIMATION

In this section we study some conditions under which the quasistatic expressions (31) and (32) might be expected to be valid. For this purpose we write

$$\psi = \sum_{\vec{k}} X_{\vec{k}} e^{-i\gamma_k(t)} \tag{37}$$

and require that this be an <u>exact</u> solution of Eq. (14). On noting the relations (4), we see that the general form of $X_{\vec{k}}$ is

$$X_{\vec{k}} = e^{i\vec{x}\cdot\vec{a}} \phi_{\vec{K}}(\vec{x}, \vec{a}, \vec{E}) \quad . \tag{38}$$

Indeed, substitution into Eq. (14) gives us the following equation for $\phi_{\vec{K}}$:

$$\left[h - e\vec{x}\cdot\vec{E} + e\vec{E}\cdot\left(\frac{1}{i}\nabla_{\vec{K}}\right) - \epsilon_K\right] \phi_{\vec{K}}$$

$$= i\left[\frac{\omega^2}{e} \vec{a}\cdot\nabla_{\vec{E}} \phi_{\vec{K}} - eE\cdot\nabla_{\vec{a}} \phi_{\vec{K}}\right] \quad . \tag{39}$$

First, let us consider the strong field limit and assume that $|\vec{a}|$ can be treated as large. Then we expect the Born approximation to be valid with h replaced by $p^2/2m$.

In this case

$$\phi_{\vec{K}} = (2\pi)^{-3/2} e^{i\vec{K}\cdot\vec{x}} \tag{40}$$

is an exact solution of the modified Eq. (39) and the adiabatic approximation is valid. Equation (40), substituted into Eq. (34), leads just to the expression used by Keldysh.

The above argument is not rigorous, since $\vec{a}$ is varying sinusoidally and must pass through zero. It does make it plausible, however, that Eq. (40) can represent a fair approximation when (eE_o/ω) is large. This is consistent with the observation of Keldysh that in this limit (and for $\omega \to 0$) Eqs. (40) and (35) lead to Oppenheimer's expression (to within a numerical factor) for ionization of a neutral atom in a static electric field.

We next use Eq. (39) to study the adiabatic approximation in the weak field limit--that is,

$$|\vec{a}| \ll k$$

--and of course continuing to assume condition (25). To do this we make an eikonal approximation for $\phi_{\vec{K}}$, writing

$$\phi_{\vec{K}} \sim e^{i\Gamma(x)}$$

$$\Gamma = \vec{K}\cdot\vec{x} - \int_{\vec{x}}^{\infty} [Q(\vec{x}') - K]\, ds\,(\vec{x}') \quad . \tag{42}$$

Since $\epsilon_k \ll I_a$, we take the eikonal trajectory to be a straight line falling into the force center. This we take to be a static potential [$-V(x)$]. The quantity Q in Eq. (42) is taken to be the positive root of

$$Q^2 = K^2 + 2mV + e\vec{E}\cdot\vec{L}_1(\vec{x}) + \vec{a}\cdot\vec{L}_2(\vec{x}) \tag{43}$$

where $\vec{L}_1$ and $\vec{L}_2$ are functions to be determined. To ensure convergence of Eq. (42), it is assumed that V (x) decreases faster than x^{-1} as $x\to\infty$. Thus, if V is a Coulomb potential, we assume it to be screened at large distances. The quasistatic approximation is valid when $\vec{L}_1$ and $\vec{L}_2$ may be neglected in Eq. (43). When $\vec{a} = 0$, Q becomes

$$Q_o = \left[k^2 + 2mV\ (\vec{x})\right]^{1/2} \quad . \tag{44}$$

If we let the eikonal trajectory lie along the Z-axis of a rectangular coordinate system, then Q = Q(Z) and $Q_o = Q_o\ (Z)$ are functions of Z only. Then

$$Q_o\ (Z) = k\left[1 + V\ (Z)/V\ (Z_o)\right]^{1/2} \tag{45}$$

where

$$V(Z_o) \equiv \epsilon_k \quad . \tag{46}$$

To first order in $\vec{a}$ and $\vec{E}$ we obtain

$$\Gamma = \Gamma_o - \vec{a}\cdot\vec{x} - e\vec{E} \cdot \int_Z^\infty L_1 dZ'/(2Q_o)$$

$$- \vec{a} \cdot \left[\int_Z^\infty \vec{L}_2 dZ'/(2Q_o) - \vec{P}_a \right] \qquad (47)$$

where Γ_o is the function Γ for $a = E = 0$ (hence, $K = k$) and

$$\vec{P}_a = \nabla_k \int_Z^\infty (Q_o - k)\, dZ' = \hat{\vec{k}} \int_Z^\infty (k/Q_o - 1)\, dZ' \equiv \hat{\vec{k}} P_a \quad . \qquad (48)$$

Substitution of Eq. (42) into Eq. (39), with the standard WKB approximation of neglecting gradients of Q, provides us with the coupled equations (valid to first order in $\vec{a}$ and $\vec{E}$)

$$L_1/(2m) = P_a - \int_Z^\infty L_2/(2Q_o)\, dZ'$$

$$L_2/2m = \omega^2 \int_Z^\infty L_1(2Q_o)\, dZ' \qquad (49)$$

where $\vec{L}_1 = \hat{\vec{k}}\, L_1$, $\vec{L}_2 = \hat{\vec{k}}\, L_2$. Use of these relations lets us re-express Eq. (47) as

$$\Gamma = \Gamma_o - \vec{a}\cdot\vec{x} + \vec{a}\cdot\vec{L}_1/(2m) - e\vec{E}\cdot\vec{L}_2/(2m\omega^2) \quad . \qquad (50)$$

The quasistatic approximation is seen to be valid when

$$L_2 \cong 0, \; L_1/(2m) \cong P_a \quad . \tag{51}$$

To integrate Eq. (49) we introduce the new variable

$$v(Z) \equiv \int_o^Z (k/Q_o)dZ'/a_o \quad . \tag{52}$$

Then

$$\frac{d}{dv}\left[L_2/(2m)\right] = -\omega\Omega L_1/(2m)$$

$$\frac{d}{dv}\left[L_1/(2m)\right] = \frac{dP_a}{dv} + a_o L_2/(2k) \tag{53}$$

where

$$\Omega \equiv m\omega a_o/k = \hbar\omega/\left[2\,(\epsilon_k R_y)^{\frac{1}{2}}\right] \quad . \tag{54}$$

The quantity (48) may be expressed in terms of v. We first define

$$\hat{P}(Z) \equiv a_o v(Z) - Z \quad . \tag{55}$$

Then

$$P_a(Z) = \hat{P}(\infty) - \hat{P}(Z) \tag{56}$$

Equation (53) may be integrated in the form

$$L_1/(2m) = P_a - \Omega \int_v^\infty \sin\left[\Omega(v' - v)\right]P_a(v')dv'$$

$$L_2/(2m) = (\omega/\Omega) \int_v^\infty \left\{1 - \cos\left[\Omega(v' - v)\right]\right\}\Gamma(v')dv' \quad . \tag{57}$$

Here

$$\Gamma(v) = \frac{d^2 P_a}{dv^2} \quad . \tag{58}$$

Alternatively, we can express L_l as

$$L_l/(2m) = \Omega^{-l} \int_v^\infty \sin[\Omega(v' - v)]\, \Gamma(v')dv' \quad . \tag{59}$$

We note from the conditions (51) that the quasistatic approximation will be valid in the limit $\Omega \to 0$ if the integral

$$\int_v^\infty P_a(v')dv'$$

is finite for all v and if the potential V is not more singular than the Coulomb potential at Z = 0.

We first study the case of a screened Coulomb potential (that is, a final ion state). Let us assume that the potential is screened at a distance R and take [see Eq. (46)]

$$Z_o = e^2/\epsilon_k \quad . \tag{60}$$

For $Z \ll Z_o$ (and $\ll R$), we obtain

$$L_1(Z)/(2m) = L_1(0)/(2m) + Z + \ldots$$

$$L_2(Z)/(2m\omega) = L_2(0)/(2m\omega)$$

$$- \frac{2}{3} (Z/a_o)^{3/2} (a_o/Z_o)^{1/2} \Omega L_1(0)/(2m)$$

$$+ \ldots \quad . \tag{61}$$

The linear Z-term in L_1 corresponds to the Reiss[6] factor $\exp(i \vec{a}\cdot\vec{x})$. The $L_1(0)$ and $L_2(0)$ terms (independent of the space coordinate) arise in satisfying the boundary condition at $|\vec{x}| = \infty$. These are time-dependent, so they will contribute to S_o [Eq. (34)]. Indeed, since $L_1(0)/2m \gg a_o$, we see no reason to neglect these terms.

When the screening radius is $R \ll Z_o$ (but $\gg a_o$), we can evaluate the relative error in the quasistatic approximation from

$$g_1 \equiv \left| \left[L_1(0)/(2m) - P_a(0) \right] / P_a(0) \right| \approx (R/a_o)^3 (\hbar\omega/Ry)^2/(12)^2 \quad . \tag{62}$$

When this quantity is sufficiently small compared to unity, we expect the quasistatic approximation to be valid.

For $R \gg Z_o$ the quasistatic approximation does not appear to be valid. Numerical evaluation of Eq. (62) gave values of g_1 and

$$g_2 \equiv \left| L_2(0)/[2m\omega\ P_a(0)] \right| \tag{63}$$

to be about unity for a wide range of parameters. Furthermore, an estimate of the second-order terms in $\vec{a}$ and $\vec{E}$, omitted from Eq. (50), indicated a contribution comparable to the first-order terms when S_o [Eq. (34)] is evaluated.

We conclude, then, that for a final ionic state, with screening distance $R \gg Z_o$, we are not able to evaluate multiphoton ionization rates. Since we have found what appear to be large corrections in the expressions used by Keldysh[5] and Reiss,[6] our confidence is not great in the accuracy of their results.

We are able to draw a more optimistic conclusion for detachment of an electron from a negative ion when the residual molecule does not have a significant permanent electric dipole moment. In this case the potential in the final state has the asymptotic form

$$-V(\vec{r}) \underset{r \to \infty}{=} -\alpha_p e^2 \Big/ (2r^4) \tag{64}$$

where α_p is the polarizability.

For photodetachment of O^- we have $\alpha_p \approx 5.29^3$ and $I_a = 1.46$ eV. Equation (67) should be numerically evaluated for a potential with the asymptotic form (64) and for small r modified to remove the singularity at r = 0. The error functions g_1 and g_2 are shown in Figure 1. The curves are labeled by N, the least number of photons required for detachment, and are given as functions of $\epsilon_k = N\hbar\omega - I_a$. As anticipated, we see that for large N, and an ϵ_k not too small, both g_1 and g_2 become small, as required for the validity of the quasistatic approximation.

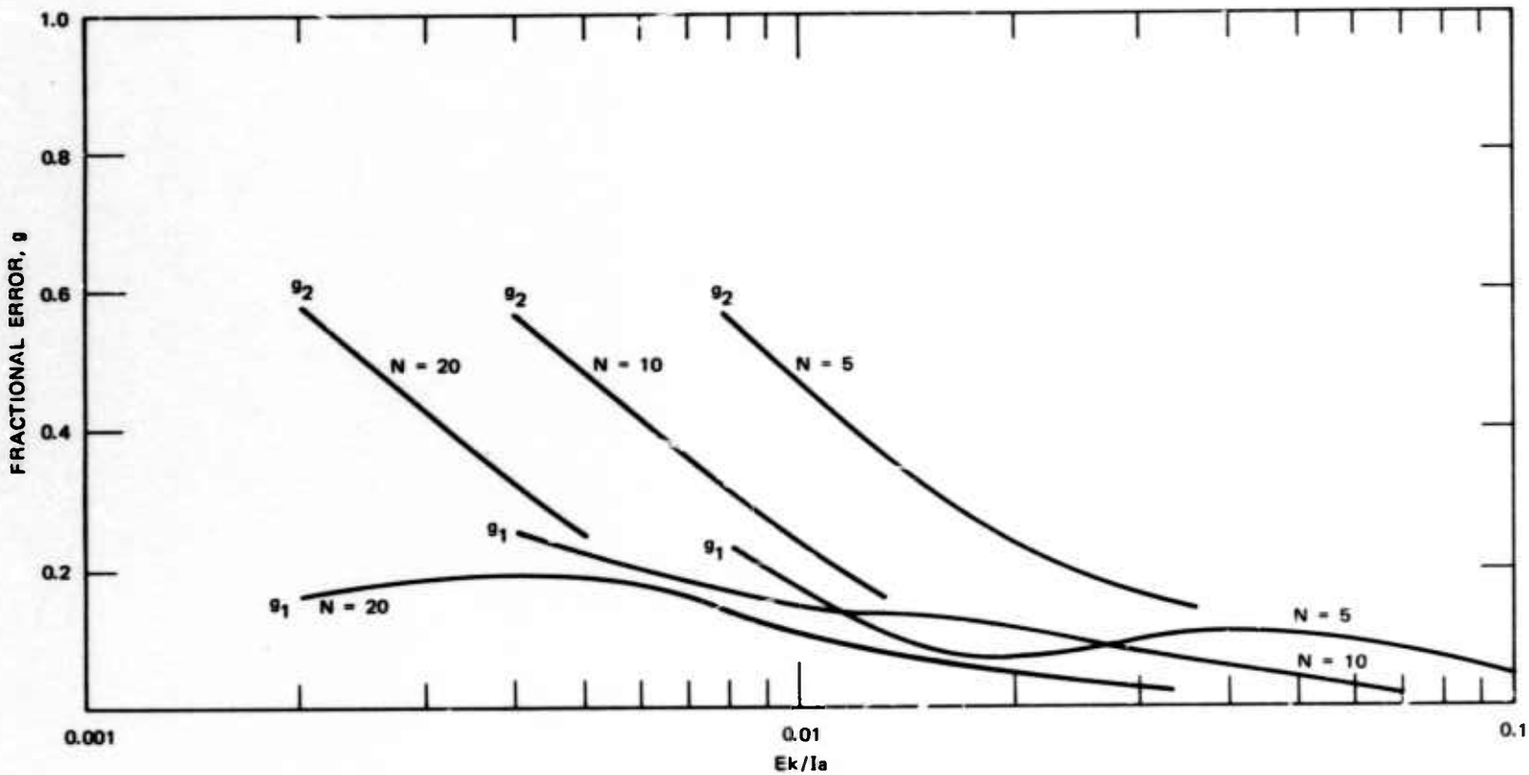

FIGURE 1 THE FRACTIONAL ERROR IN THE QUASI-STATIC APPROXIMATION [Functions (62) and (63)] SHOWN AS A FUNCTION OF THE FINAL ELECTRON ENERGY FOR 5-, 10-, AND 20-PHOTON DETACHMENT OF O^-. The curves for g_2 are continued only to the g_1 curves to simplify the drawing.

V DETACHMENT OF 0^-

We now use the expression (34) to evaluate the multiphoton detachment rate of 0^- in the weak field limit. The single photon detachment rate has been studied experimentally by Branscomb et al.[9] Theoretical studies have been made by Brueckner and Klein[10] and by Gillespie.[11] Since the attached electron is in a p-orbital state the transition will take place to a state of zero angular momentum if the electron energy is sufficiently low. We thus use condition (25) to write[11]

$$\left(\phi^-_{\vec{K}}\,,\ e\,\vec{x}\,\phi_a\right) E_o \simeq f^{-1}(-K)\, CE_o \tag{65}$$

where C is a constant and f is the Jost function which we write in the effective-range approximation as*

$$f^{-1}(-K) = (K + ia)/(K + ib) \quad . \tag{66}$$

Here a and b are constants related to the scattering length and effective range for electron scattering by a neutral oxygen atom.†

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* See, for example, Ref. 7, p. 540.

† T. F. O'Malley et al.[12] have shown that for a potential having the asymptotic form (64) the effective range expansion is modified. For the very low electron energies of interest to us this modification is not significant.

Following Keldysh,[5] we take $\phi_o = \frac{\pi}{2}$ and introduce the variable $u \equiv \sin \omega t$ in Eq. (34). We shall assume that the electromagnetic field is weak in the sense that

$$(eE_o/\omega) \ll k \quad . \tag{67}$$

We rewrite (34) in the form

$$S_o = -(2\pi)^{-1} \left[\oint \frac{du}{f(-K)} \, e^{iQ(k,u)} \right] CE_o \quad . \tag{68}$$

Here the closed contour encloses the points $u = -1, 1$ and lies within any other singularities of e^{iQ}/f.

In the weak field limit we can deform the contour so that everywhere on it $|u| \gg 1$. An elementary evaluation gives us, then,

$$e^{iQ} = (i/2)^N \exp(-\beta u^2/4) \exp\left[-e\vec{k}\cdot\vec{E}_o u/(m\omega^2)\right] u^{-N} \ , \ |u| \gg 1 \quad . \tag{69}$$

Here

$$N = \left[I_a + \epsilon_k + e^2 E_o^2/(4m\omega^2) \right] /(\hbar\omega)$$

is, according to Eq. (35), the number of photons required to detach the excess electron, and $\beta = \left[e^2 E_o^2/(m\omega^2) \right] /(\hbar\omega)$.

As Keldysh observed,[5] Eq. (69) has two saddle points at the roots of

$$I_a + \frac{1}{2m} K^2 = 0 \quad . \tag{70}$$

These correspond to*

$$u_s \cong \pm i\gamma \equiv \pm i\omega\sqrt{2mI_a}/(eE_o) \quad . \tag{71}$$

As also observed by Keldysh, the expression (65) has poles at the positions defined by (70). The quantity C. in Eq. (65), which is really K-dependent, has poles at the same positions.[11]

Keldysh used the Born approximation, so in his expressions, f = 1. He was thus able to evaluate (68) keeping only the contribution from the saddle points at $u_s \cong \pm i\gamma$.

We cannot use the Keldysh approximation because $f^{-1}(-K)$ has branch points at

$$u_b = \omega(-k_\parallel \pm ik_\perp)/(eE_o) \tag{72}$$

where $k_\parallel$ is the component of $\vec{k}$ parallel to $\vec{E}_o$, and $\vec{k}_\perp$ is the component of $\vec{k}$ perpendicular to $\vec{E}_o$. Since $|u_b| \ll |u_s|$ our integral (68) will receive its principal contribution from the vicinity of the branch points. The contour of integration used is shown in Figure 2.

Evaluation of (68) is straightforward when N is large. The rate of detachment is, finally, in the limit of large N:

$$R = 2\pi \int d^3k\,\delta\left(I_a + \epsilon_k + e^2E_o^2/(4m\omega^2) - N\hbar\omega\right)|S_o|^2$$

$$\cong \frac{\omega}{2\pi}\left[\sigma_1(k)/a_o^2\right]\left[k\left(\frac{1}{b} - \frac{1}{a}\right)\right]^2\left[\frac{\epsilon_k}{2\alpha N^3 Ry}\right]$$

$$\times\, U(2\epsilon_k/\hbar\omega)\left[eE_o/(2k\omega)\right]^{2N} \tag{73}$$

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* Equation (71) would be exact if $\vec{k}$ were zero. For nonvanishing k the actual saddle points are displaced slightly from the position ± i γ.

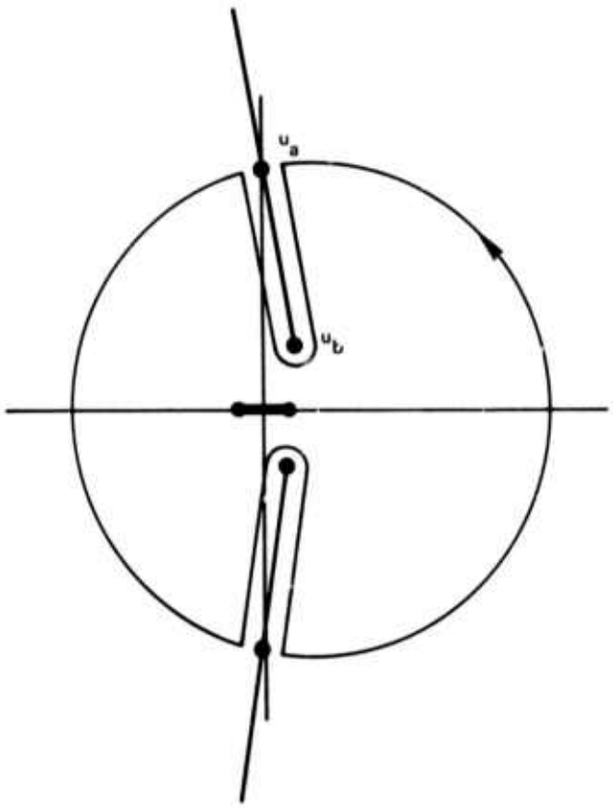

FIGURE 2 CONTOUR OF INTEGRATION FOR THE INTEGRAL (68), SHOWING THE TWO BRANCH POINTS u_b AND THE TWO SADDLE POINTS u_s. Branch lines are indicated between u = -1 and +1 and from $\pm u_b$ to $\pm u_s$.

In the lower version of this equation, k is evaluated when the argument of the δ-function vanishes, α is the fine-structure constant, and R is the Rydberg constant. We have expressed R in terms of the cross section $\sigma(k)$ for detachment by a single photon of energy $\hbar\omega_1 = I_a + \epsilon_k$. Finally,

$$V(x) \equiv \frac{e^{\frac{x}{2}}}{n} \int e^{x\cos^2\theta} \sin^2\theta \, d\theta \quad . \tag{74}$$

The ionization rate (73) is illustrated in Figure 3 as a function of laser power density [expressed in watts/cm^2] for several values of the photon energy $\hbar\omega$ using the experimental values of σ_1 from Ref. 9. We note that our result (73) is substantially different than that which would be obtained from the Keldysh evaluation using the Born approximation.

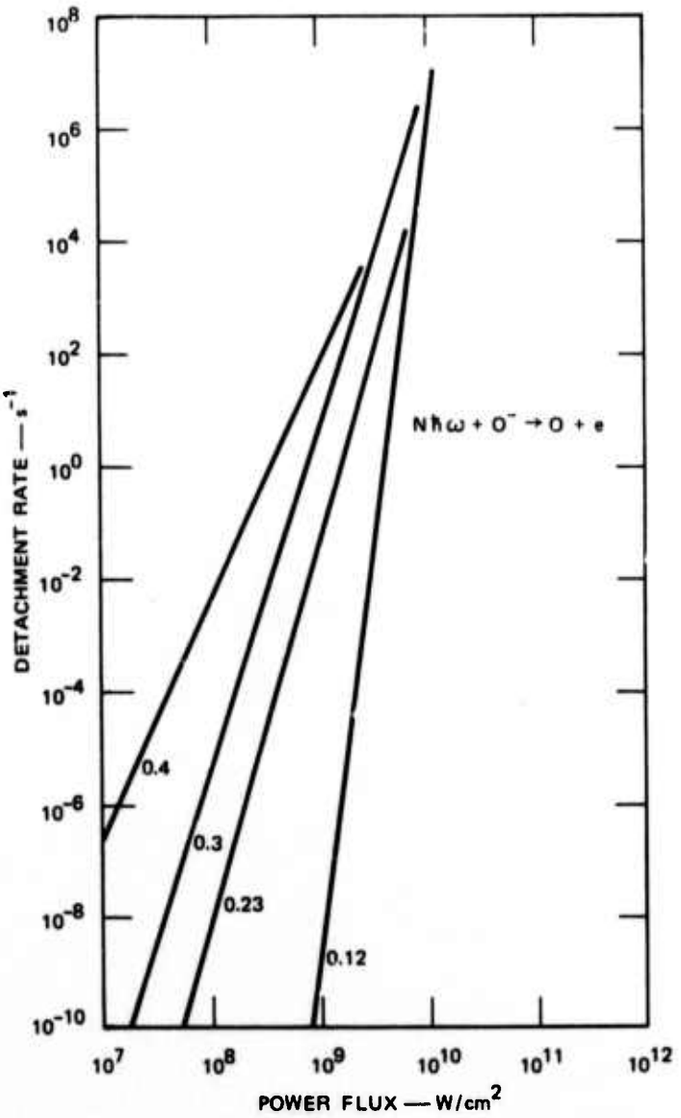

FIGURE 3 THE DETACHMENT RATE (73) FOR O^- SHOWN AS A FUNCTION OF THE LASER-BEAM POWER FLUX. The curves are labeled by the photon energy in electron volts.

It is interesting to observe that for large photon numbers the cross section (73) is considerably enhanced for electrons near threshold. Our weak field approximation (67) fails for very low electron energies, however, and the apparent divergence of Eq. (73) at $k = 0$ is due to the failure of this approximation.

VI DETACHMENT OF O_2^-

Cross sections for photodetachment of O_2^- have been published by Burch et al.[13] The detachment energy is $I_a = 0.44$ eV and the electronic configuration is a $^2\Pi_g$ state. An electric-dipole transition cannot take place to a final S-state for the $^2\Pi_g$ state. Geltmann[14] has discussed the implications of this for the near-threshold dependence of the single-photon detachment cross section.

A theory of final-state enhancement does not seem to have been given for nonspherical potentials. Until such a theory is available, we shall use Eq. (73) with an appropriate shift of parameters. For $\sigma_1(k)$ we shall take the experimental value of Burch et al.[13] This is admittedly not a rigorous theory. If, however, the dipole matrix element has the branch points (72) as closest to the origin in the μ-plane, the ionization rate is rather insensitive to other details of the matrix element.

The resulting ionization rate as a function of laser power is shown in Figure 4 for 10.6-μm radiation.

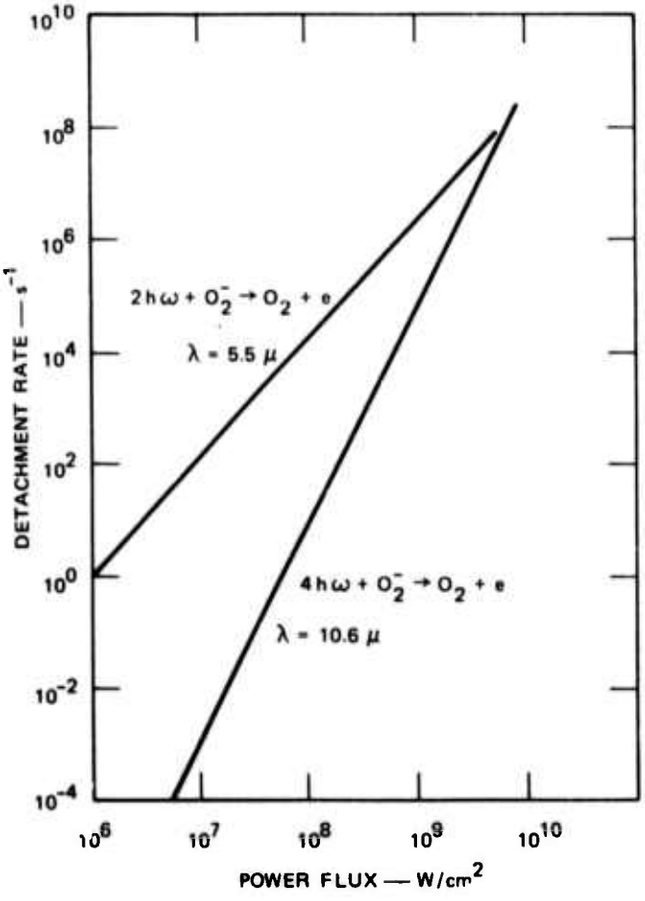

FIGURE 4 THE DETACHMENT RATE FOR O_2^- SHOWN AS A FUNCTION OF LASER-BEAM POWER FOR WAVELENGTHS OF 10.6 AND 5.5 μm

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