Electric Quadrupole Transitions in Multiphoton Ionization*

P. Lambropoulos, Gary Doolen, and Steven P. Rountree
Physics Department, Texas A & M University, College Station, Texas 77843

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It is shown that even for optical frequencies the dipole approximation is not always valid in multiphoton ionization. For certain photon frequencies, we find quadrupole-dipole contributions which are several orders of magnitude larger than the usual dipole-dipole contribution to two-photon ionization.

Multiphoton transitions in atoms have up to now been calculated in the electric dipole approximation. In this Letter, we show that for certain photon frequencies there are significant contributions from electric quadrupole transitions which exceed the dipole contributions by several orders of magnitude. As a result, multiphoton ionization cross sections will not necessarily exhibit some of the deep valleys found in calculations based solely on the dipole approximation.[1,2]

In many cases instead of deep valleys one will observe sharp peaks. For this to occur, the photon frequency must be approximately equal to the energy difference between two states connected via a quadrupole transition. Examples would be multiphoton processes of the type: $nS \xrightarrow{(Q)} n'D \to \vec{K}$, $nS \to n'P \xrightarrow{(Q)} n''P \to \vec{K}$, $nS \to n'P \xrightarrow{(Q)} n''F \to \vec{K}$, etc., where $\vec{K}$ denotes a continuum state. The symbol (Q) indicates the quadrupole transition. In addition, the nearest state for which a dipole transition is allowed must be sufficiently far from resonance so that the smallness of the quadrupole matrix element is compensated for by the respective energy denominator. A more precise statement of this criterion will be given after a quantitative discussion of a specific case.

To present a quantitative case, we first discuss in detail two-photon ionization of atomic Li. In the perturbation-theory regime, the total transition probability per unit time is obtained from the equation[3]

$$W_{fi} = 2\pi \left| \textstyle\sum_j V_{fj} V_{ji} (\omega_j - \omega_i)^{-1} \right|^2 \delta(\omega_f - \omega_i), \qquad (1)$$

where $|i\rangle$ and $|f\rangle$ are the initial and final states, respectively, with energies $\hbar\omega_i$ and $\hbar\omega_f$. The sum is over all intermediate states and V is the interaction between radiation field and atom.[3] These states are to be understood as states of the system "atom plus field." The interaction V can be written in terms of the multipole expansion[4]

$$\begin{aligned} V &\equiv V^D + V^Q + \dots \\ &\equiv -e\vec{r}\cdot\vec{\mathcal{E}}(0) - \tfrac{1}{2}e\textstyle\sum_{ij} Q_{ij}\nabla_j \mathcal{E}_i(0) + \dots, \end{aligned} \qquad (2)$$

where e is the electronic charge, $\vec{r}$ the position operator of the electron undergoing the transition, and $\vec{\mathcal{E}}(0)$ the electric field evaluated at the origin of the system of coordinates—the position of the nucleus. Q_{ij} is the quadrupole dyadic[4] defined by

$$Q_{ij} = x_i x_j - \tfrac{1}{3} r^2 \delta_{ij}, \quad i, j = 1,2,3, \qquad (3)$$

where $r^2 = x_1^2 + x_2^2 + x_3^2$ (with the usual identification $x_1 = x$, $x_2 = y$, $x_3 = z$) and δ_{ij} is the Kronecker delta. The first term V^D in Eq. (2) is the usual electric dipole contribution while the second term is the electric quadrupole contribution to the interaction. Higher-order electric multipoles and magnetic multipoles contribute negligibly to the type of transitions studied in this paper. For more complicated atoms, magnetic dipole transitions may also have to be considered in some cases.

The usual dipole contribution to W_{fi} is obtained by taking $V = V^D$ in Eq. (1). Consider, however, two-photon ionization of Li with photons of energies $\hbar\omega \approx E_{3d} - E_{2s}$, where E_{nl} is the energy of the atomic state $|nl\rangle$ (we neglect spin-orbit coupling for the moment). Since the nearest p state is $|3p\rangle$ which is about 358 cm^{-1} away from $|3d\rangle$, the dipole contribution to two-photon ionization will be due to off-resonance (virtual) transitions. Because of interference between the various $2s \to np$ contributions, the generalized cross section[5] $\hat{\sigma}$ drops to a rather small value[1,2] for the above photon energies. ($\hat{\sigma} \approx 10^{-51}$ cm^4 sec). Noting that the electric quadrupole transition $2s \to 3d$ is allowed, one may ask whether two-photon ionization via the channel $2s\text{-}(V^Q) \to 3d\text{-}(V^D) \to \vec{K}$ might not in fact be more probable than the dipole-dipole transition. $\vec{K}$ is the wave vector of the outgoing photoelectron.

We take light linearly polarized along the z axis and propagating along the x axis, so that we can compare the result with existing calculations for the dipole-dipole contribution. The quadrupole-dipole contribution is obtained from Eq. (1) by taking $V_{ji} = V_{ji}^{Q}$ and $V_{fj} = V_{fj}^{D}$. Following a procedure which has been presented in detail elsewhere,[3] we obtain

$$\hat{\sigma} = 2\pi(2\pi\alpha)^2\hbar\omega^2 \int |M|^2 \, d\Omega_{\vec{\mathrm{k}}}, \tag{4}$$

where

$$M \equiv \frac{\langle \vec{\mathrm{K}} | z | 3d\rangle \frac{1}{2} k \langle 3d | zx | 2s\rangle}{\omega_{3d} - \omega_{2s} - \omega + i\Gamma_{3d}}; \tag{5}$$

$|\vec{\mathrm{K}}\rangle$ represents the continuum state of the photoelectron, $k = \omega/c$ is the wave vector of the incident photons of frequency ω, $\hbar\omega_{nl} = E_{nl}$ are atomic state energies, Γ_{3d} is the appropriate width for the state $|3d\rangle$, and α is the fine-structure constant. In Eq. (5) we have only one term—instead of a whole sum over intermediate d states—because we are considering a near-resonance process. Because of the smallness of the quadrupole matrix elements, the contribution of off-resonance d states is negligible compared with the dipole-dipole background. Note that Eq. (5) looks very much like the corresponding dipole-dipole expressions[1-3] except that we have $\frac{1}{2}k\langle 3d| \times zx|2s\rangle$ instead of $\langle np|z|2s\rangle$. There are of course differences in the numerical coefficients arising from the angular momentum algebra. The expression for M as used in Eqs. (4) and (5) is independent of the normalization of the continuum states because it contains the density of final states.

After some angular momentum algebra, the above matrix elements are reduced to expressions involving radial matrix elements. Thus we obtain

$$\int |M|^2 d\Omega_{\vec{\mathrm{k}}} = \tfrac{1}{75} \times \tfrac{1}{4} k^2 |\langle 3d | r^2 | 2s\rangle|^2 \left(\tfrac{8}{7} |\langle KF | r | 3d\rangle|^2 + |\langle KP | r | 3d\rangle|^2\right) [(\omega_{3d} - \omega_{2s} - \omega)^2 + \Gamma_{3d}{}^2]^{-1}, \tag{6}$$

where $|KF\rangle$ and $|KP\rangle$ denote the radial parts of the F and P partial waves in the expansion of the continuum state in spherical harmonics. We have obtained values for these radial bound-free matrix elements by using a close-coupling calculation in the static-exchange approximation. The details of this calculation, as well as results for a number of bound-free transitions, will be published elsewhere.[6] Their values are $|\langle KP | r | 3d\rangle| = 0.276 a_0/\sqrt{\mathcal{R}_\infty}$ and $|\langle KF | r | 3d\rangle| = 1.056 a_0/\sqrt{\mathcal{R}_\infty}$, where $a_0 \cong 5.29 \times 10^{-9}$ cm is the Bohr radius. These values correspond to a photoelectron energy of about 0.18 Ry, which is the case for two-photon ionization of Li with photons of energy $\hbar\omega \approx E_{3d} - E_{2s} \cong 31\,283$ cm^{-1}. This frequency can be obtained, for example, as the second harmonic of a rhodamine dye laser. The quadrupole matrix element has been calculated most recently by Caves.[7] Its value is $\langle 3d | r^2 | 2s\rangle = -19.39 a_0{}^2$.

Using the above values, we obtain

$$\hat{\sigma} = 0.917 \times 10^{-57} \xi^2 \text{ cm}^4 \text{ sec}, \tag{7}$$

where $\xi^2 \equiv \omega^2/[(\Delta\omega)^2 + \Gamma_{3d}{}^2]$ and $\Delta\omega \equiv \omega - (\omega_{3d} - \omega_{2s})$. The quantity ξ^2 gives the dependence of $\hat{\sigma}$ on the photon frequency around the $2s \to 3d$ quadrupole resonance. The fine-structure splitting of $|3d\rangle$ is about 0.04 cm^{-1}, while its natural width is of the order of 0.5×10^{-3} cm^{-1}. Therefore as long as $\hbar\omega$ is about 0.1 cm^{-1} or more away from resonance, fine-structure and width can be neglected. The value of $\hat{\sigma}$ is then obtained by simply taking $\xi^2 = (\omega/\Delta\omega)^2$. For $\hbar(\Delta\omega) = 0.1$, 1.0, and 10.0 cm^{-1}, we find $\hat{\sigma} = 0.893 \times 10^{-46}$, 0.893×10^{-48}, and 0.899×10^{-50} cm^4 sec, respectively. The dipole-dipole contribution to $\hat{\sigma}$ in this frequency range, as calculated in Refs. 1 and 2, is smaller than 5×10^{-51} cm^4 sec. For $\Delta\omega = -|\Delta\omega|$ the value of $\hat{\sigma}$ will be slightly smaller than for $+|\Delta\omega|$, because ω will be smaller, but we can disregard this difference for the present discussion.

We have shown therefore that for a range of photon frequencies of about 50 cm^{-1}, the quadrupole-dipole contribution to two-photon ionization of Li is larger than the usual dipole-dipole contribution. Within a few wave numbers from the $2s \to 3d$ resonance, the quadrupole-dipole term will dominate by about 2 orders of magnitude. Thus instead of the deep valley found in Refs. 1 and 2 for $\hbar\omega \approx 31\,283$ cm$^{-1} \approx 3.9$ eV, $\hat{\sigma}$ will exhibit a sharp peak. Even more important, the values of $\hat{\sigma}$ in that frequency range represent rather substantial two-photon ionization generalized cross sections which makes these quadrupole contributions readily observable with present-day tunable dye lasers. Recall that the two-photon ionization rate (neglecting photon-statistics effects) is given by $\hat{\sigma} I^2$, where I is the photon flux in number of photons square centimeter per second. As an example, take $I = 10^{26}$; for $\hat{\sigma} \simeq 10^{-46}$ and a laser pulse duration of the order of 100 nsec, about 1% of the atoms in the interaction region will be ionized during the laser pulse.

It is now evident that quadrupole-dipole contributions will be significant in alkali-like atoms whenever the photon frequency is such that $\hbar\omega \approx E_{n'd} - E_{ns}$ provided there are no p states near the $|n'd\rangle$ state. An order-of-magnitude criterion can be obtained by comparing $R_{n'd}{}^Q \equiv \frac{1}{4}k^2 |\langle n'd| r^2 \times |ns\rangle|^2$ with the dipole matrix element $R_{n''p}{}^D \equiv |\langle n''p| \times r |ns\rangle|^2$, where $|n''p\rangle$ is the p state nearest to $|n''d\rangle$, and $k = (E_{n'd} - E_{ns})/\hbar c$. Normally, we shall have $R_{n'd}{}^Q / R_{n''p}{}^D \ll 1$. For example, in the case of Li discussed above, this ratio (with $n' = 3$ and $n'' = 3$) is about 2.16×10^{-3}. The quadrupole-dipole contribution will be significant when $|n''p\rangle$ is sufficiently far from $|n'd\rangle$ for the ratio $(E_{n''p} - E_{ns} - \hbar\omega)^2 / (E_{n'd} - E_{ns} - \hbar\omega)^2$ to compensate for the smallness of $R_{n'd}{}^Q / R_{n''p}{}^D$ [see Eq. (5)]. This is an approximate criterion because it does not account for differences in angular momentum factors or in the bound-free matrix elements. The dipole-dipole contribution is further reduced for certain ranges of frequencies because of cancelation of positive and negative contributions arising from the opposite signs of the energy differences in the denominators. This makes the relative contribution of the quadrupole transition more significant: In the case of Li, as one considers nd states higher than the $3d$, the quadrupole matrix elements $2s \to nd$ decrease,[7] but so do the $2s \to np$ dipole matrix elements. What eventually limits the importance of the quadrupole-dipole contribution is the fact that the energy difference between p and d states decreases with increasing n. As a result, above some n the quadrupole-dipole contribution becomes smaller than the dipole-dipole background. Exactly where this happens will also depend on the linewidth of the laser. We also mention in passing that the photoelectron angular distribution of the quadrupole-dipole contribution will be different from that of the dipole-dipole contribution. The highest power of $\cos\vartheta$ will be $\cos^6\vartheta$ in the former and $\cos^4\vartheta$ in the latter; ϑ is the angle between the light polarization vector and the electron wave vector $\vec{K}$.

Considering now briefly the other alkalis one finds the situation to be largely the same. The energy differences $E_{n'd} - E_{ns}$ (where $|ns\rangle$ is the ground state) decrease with increasing Z, but on the other hand the matrix elements increase. The end result is that the quadrupole-dipole contributions—for the first few $ns \to n'd$ transitions—will be significantly higher than the dipole-dipole contributions for certain photon frequency ranges. Such frequencies are readily obtained with a tunable dye laser or the second harmonic thereof. The necessary linewidths are of the order of one to a few wave numbers, depending on the particular atom and transition under consideration. In any case, these are frequencies and linewidths used presently in two-photon spectroscopy. For sufficiently narrow laser linewidths, one must also take into account fine structure. This is an interesting side of the problem but space does not permit its discussion here.

Our results have several implications. First, two-photon ionization rates for certain photon frequencies will be higher than theoretical rates based on the dipole approximation. This will also occur in higher-order processes. Second, multiphoton processes can provide information on on bound-bound electric quadrupole—or perhaps even higher multipole—transitions.

Third, the following question arises: How valid is it simply to adopt the dipole approximation in multiphoton calculations? We have shown that in the perturbation-theory limit this is not always valid. Consequently, certain methods[8-10] cannot give the correct result whenever a quadrupole resonance contributes. Note that it is the dipole approximation that enables such methods to obtain analytic solutions. Further, it would seem that even in the ultrastrong-field limit[11,12] the dipole approximation may break down. One can see how this might come about by considering an electron in a field so strong that the atomic potential could at first be neglected. Then the Lorentz force law gives $m\vec{a} = -e[\vec{E}(\vec{r},t) + (\vec{v}/c) \times \vec{B}(\vec{r},t)]$, where the electric field $\vec{E}$ can for simplicity be taken as $\vec{E}(\vec{r},t) = \vec{E}_0 \cos(\vec{k}\cdot\vec{r} - \omega t)$ with a similar expression for the magnetic field $\vec{B}(\vec{r},t)$. As long as the field is not too strong, the acceleration $\vec{a}$ is small and $(\vec{v}/c) \times \vec{B}$ can be neglected. In that case, the acceleration, velocity, and displacement of the electron remain parallel to $\vec{E}$. This implies that $\vec{k}\cdot\vec{r} \approx 0$ which is equivalent to the dipole approximation. It is known[13] however that for intensities sufficiently large, an unbound electron experiences Compton scattering[14] which means it experiences a net force along $\vec{k}$. This contradicts the dipole approximation. Consequently, above a certain field intensity all multipoles would be important. At such intensities, the electron interacts with the field over distances of the order of one wavelength or more.

Nevertheless there may be a regime of intensities which are stronger than the atomic binding potential, yet not sufficiently strong for Compton scattering to be significant. In that regime, the dipole approximation should be valid as long as the atomic structure has no effect. It is not our intention to dismiss unconditionally the validity of the dipole approximation in multiphoton processes. Clearly it will be valid under a wide range of circumstances. We do however wish to point out that its validity is not as general as has been assumed on the basis of the usual argument that for optical wavelengths the dipole approximation is valid. Although this is correct for weak fields, in the presence of strong fields and multiphoton processes the argument loses its generality.

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Observation of Anomalously Large Supercooling in Carbon Dioxide*

John S. Huang and W. I. Goldburg
University of Pittsburgh, Department of Physics, Pittsburgh, Pennsylvania 15260

and

M. R. Moldover
Institute for Basic Standards, National Bureau of Standards, Washington, D. C. 20234

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We have observed supercooling in liquid CO_2 near the critical temperature greatly exceeding that allowed by existing theories of homogeneous nucleation.

We report here a calorimetric study of nucleation in *liquid* carbon dioxide (CO_2). We have clearly observed that in the vicinity of the critical point, CO_2 may be "supercooled" at constant density to temperatures well below those at which homogeneous nucleation of vapor bubbles is predicted to occur by current theories.[1-5] Some hint of this anomalously large supercooling in the critical region of CO_2 is apparent in earlier calorimetric experiments by Straub[6] and in experiments where nucleation was observed visually.[7] Anomalously large supercooling has also been found near the critical point of the binary liquid mixture C_7H_{14}-C_7F_{14} by Sundquist and Oriani[8] and by Heady and Cahn.[9] These earlier experiments, reinforced by the present one, indicate that there is a serious gap in our understanding of nucleation in fluids near their critical points.

We have made three other significant observations: (1) Supercooling could be achieved only in samples filled to a density greater than the critical density, ρ_c. (2) Repeated runs with a given density, ρ, yielded identical nucleation temperatures when ρ was near ρ_c but a wide distribution