Energy Partition among Fragments and Electrons in High Field Dissociation

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We present an experimental investigation for chlorine molecules and their atomic fragments in which high field molecular dissociation is followed by fragment ionization. It is shown that the intensity dependence of the photoelectron and atomic photofragment energy spectra provides a direct measure of the fragments' ac-Stark shift. Furthermore, we observe an unusually strong above-threshold ionization photoelectron series associated with the two-photon ionization of the excited chlorine fragment. This implies that the fragments are experiencing field strengths in excess of the "low field" saturation intensity. These results are compared to a single-channel quantum-defect calculation.

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It is well understood that under proper laser frequency and intensity conditions, atomic energy levels and ionization potentials (IP) shift [1]. Except for the very short pulses [2], these changes are usually not directly measurable due to the energy gained by the freed electron as it slides down the laser field gradient via ponderomotive acceleration [3]. Thus, the net change in detected electron energy is zero under adiabatic conditions, i.e., when the laser intensity is changing at a rate slow compared with the electron travel time through the interaction region. Both ponderomotive suppression and ac-Stark-shifted resonances [1,2] are good indications of energy levels shifting proportional to the laser intensity. The shift of energy levels results in similar effects in the case of molecular ionization [4]. Moreover, if molecules can dissociate through one of these states, this same shift should also influence the kinetic energy of the dissociating fragments. We report in this Letter the observation of laser-intensity-dependent changes in the atomic fragments' kinetic energy which have not been reported to date.

In this paper, we will present an investigation of the high field physics associated with the scenario in which both the dissociation of the molecule and the subsequent ionization of the neutral atomic fragments originate from the same superexcited molecular potential. This study focuses on the effect the molecule-field interaction has on the redistribution of energy from ponderomotive or ac-Stark shifts among the electrons, the nuclear fragments, and the field. An experimental study of chlorine molecules and fragments will be presented and interpreted within this framework. This differs from previous studies [4] which treated ionization and dissociation processes separately. Moreover, since the dissociation process is quite nonlinear, the excited atoms that are formed experience intense radiation fields higher than the "low field" saturation intensity. The low field saturation is defined as the maximum intensity an isolated atom can experience before it becomes ionized and is dependent upon the dynamics of the laser pulse [5]. This low field saturation problem has become more relevant in connection with the prospects of observing intense field stabilization. One way to counter this problem is the use of extremely short laser pulses (few fsec) [2] to increase the saturation flux. Another technique has been demonstrated separately by Jones and Bucksbaum and by Stapelfeldt *et al.* [6]. They have found that the relationship between the Rydberg orbit time and pulse duration can effectively stabilize states against ionization. We, on the other hand, demonstrate in this Letter that if the atoms are formed as a result of a highly nonlinear molecular dissociation process, the laser field reaches its peak value by the time the subsequent ionization takes place, thereby avoiding the problem of premature ionization. Thus, a *molecular precursor* affords the opportunity to study atoms in unusual circumstances.

Second-harmonic radiation from two different laser systems, described elsewhere in detail [7,8], are used. One of these is a 10-nsec *Q*-switched Nd:YAG and the other is a 50-psec Nd:YLF regenerative amplifier generating 1064- and 1053-nm pulses, respectively, in the intensity range 5×10^{11} to 5×10^{13} W/cm^2. The two lasers aid in the assignments since we are able to study the molecule at two slightly different wavelengths and saturation conditions. The investigations consisted of time-of-flight (TOF) electron and mass spectroscopy under ultrahigh vacuum conditions. Complete data sets were taken at both wavelengths and resulted in similar TOF structure. Excited Cl atoms were prepared by the five-photon excitation of Cl_2 above the ionization limit, as shown in Fig. 1. At this point the superexcited $[Cl_2]^*$ molecules can ionize or dissociate with similar rates [9] due to the details of continuum structure. Direct neutral dissociation occurs via the $3\,^3\Pi_u$ Rydberg state which has been identified [9] to converge onto the $A\,^2\Pi_u$ ionic state, producing chlorine atoms in the ground and excited ^4P_J $(3s^23p^44s)$ states. Once the ^4P_J state of the Cl atom is formed, it can subsequently ionize, producing a photoelectron.

Figure 2 shows the photoelectron spectrum of Cl_2 at 3×10^{12} W/cm^2. The molecular ions which are formed via five-photon ionization dominate the total population (lowest-energy peaks). The six-photon and higher-order

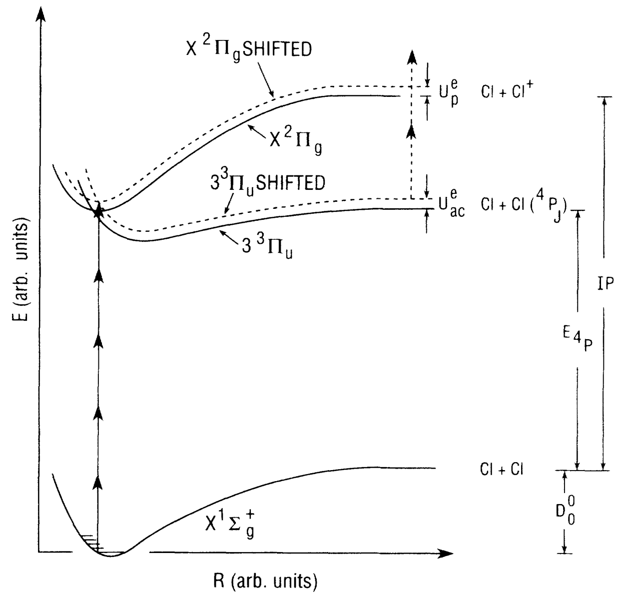

FIG. 1. Some relevant potential energy curves for chlorine molecule and their dissociative limits. The terms labeled are those relevant to equations in text. The dashed lines are the field-shifted potential curves. For simplicity, the ac-Stark shift is shown independent of internuclear distance but the field shifts could be R dependent.

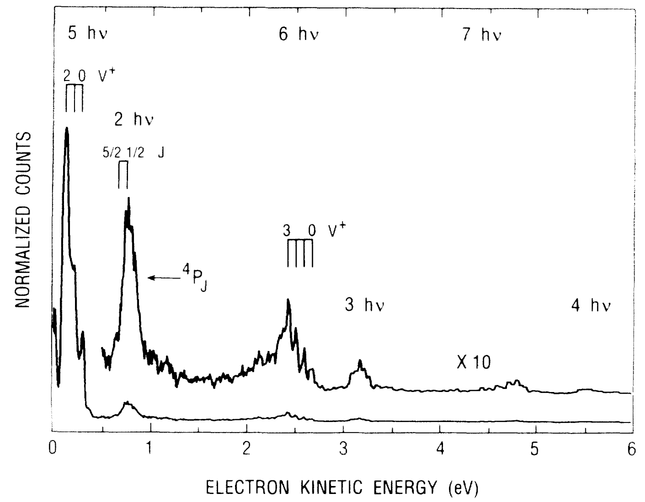

FIG. 2. Photoelectron spectrum of chlorine with 527 nm radiation at 3×10^{12} W/cm^2. Tick marks above the ^4P_J peak show expected electron energy peaks from the unperturbed J levels while the molecular peaks show the different unperturbed vibrational states of the $\mathrm{Cl_2}^+$ ground state.

above-threshold ionizations (ATI) of Cl_2 are observed with relatively lower magnitude. At the highest intensities (not shown), the electron spectrum shows a series of peaks assignable to the six-photon ionization and associated ATI of ground-state atomic chlorine. Details of these transitions will be discussed in a future more detailed paper. The most interesting part of the spectrum, however, are the relative amplitudes and positions of the peaks at 0.77, 3.13, and 5.49 eV, originating from the two-, three-, and four-photon ionizations of the excited-state (^4P_J) Cl atoms. These peaks are found to be shifted towards higher energies and the magnitude of the shifts varies approximately linearly with laser intensity, as shown for the lowest-energy peak (open circle) in Fig. 3.

Ionization of ^4P_J Cl atoms requires an absorption of two photons and the unshifted electrons that emerge have kinetic energies of 0.67, 0.73, and 0.77 eV from $J=\frac{5}{2}$, $\frac{3}{2}$, and $\frac{1}{2}$, respectively. These independent peaks form a contour due to the limited resolution of our spectrometer and due to the spatial averaging of the laser intensity distribution in the interaction volume. We have simulated the profile of this contour assuming statistically populated fine-structure components, a Gaussian line shape for individual peaks, and a spectrometer resolution of 60 meV. The maximum from simulation occurs at 0.69 eV whereas our spectra show electrons at higher energies. If ^4P_J Cl is assumed to be populated in a single J, e.g., the $J=\frac{5}{2}$ level only, the experimental shifts in Fig. 3 will become larger by 10% to 20%. Moreover, our simulations give a linewidth of 115 meV (FWHM) for the ^4P_J peak compared with the experimentally observed width of 120 meV. The widths of similar energy peaks in xenon were found to give a spectrometer resolution of 60 meV. This additional broadening supports the assumption of a distribution of fine-structure states.

Figure 4 shows the TOF mass spectrum of Cl atoms formed via dissociation of a Cl_2 molecule through the

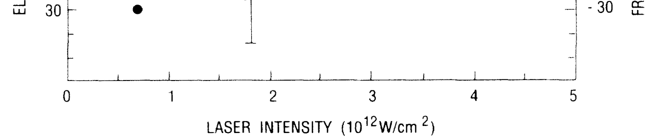

FIG. 3. Photoelectron (open circles) and ^4P chlorine fragment (solid circles) kinetic energy shifts as a function of 527 nm laser intensity. The typical error associated with the electron and mass spectrometer measurements are shown by the vertical bars. The dashed line shows the calculated SQDT ac-Stark shift of the Cl atom's ^4P state. The solid line results assuming a pure ponderomotive shift and provides a line of reference for the reader.

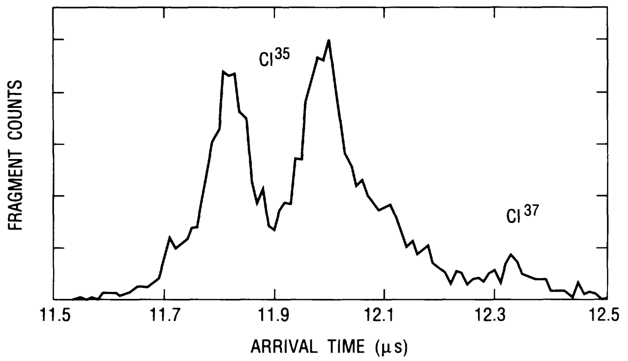

FIG. 4. The TOF mass spectrum of chlorine (^{35}Cl) results from dissociation of Cl$_2$ through the $3^3\Pi_u$ state with 532 nm radiation at 6.7×10^{11} W/cm^2. The shoulder of the peak originates from the dissociation of isotopically substituted chlorine molecules. The splitting of the peak arises due to the turnaround times associated with the forward and backward moving fragments and is directly related to the fragments' kinetic energy; see, for instance, Ref. [4]. The laser polarization is parallel to the time-of-flight tube axis. The 527-nm mass spectrum (not shown) is qualitatively similar.

$3^3\Pi_u$ state at 6.7×10^{11} W/cm^2, which is consistent with our electron assignment. *The total Cl fragment kinetic energy was also observed to shift with increasing intensity but towards lower energies,* as shown by the solid circles in Fig. 3 (note that the left and right ordinate axes have opposite signs). However, due to the lower resolution of the mass spectrometer the uncertainty is larger compared to the electron data. We are unable to assign any other transition that will result in electrons and ions with the observed energy distributions. In addition, we have also systematically eliminated the possibility of space charge and contact potentials as sources of this shift. Above all, other peaks in the spectra do not seem to be affected by these shifts. We should mention that at our final state energy, an assignment consistent with ours has been made by Koenders *et al.* [9] in their (2+1) resonance enhanced multiphoton ionization and photoelectron spectroscopy studies of chlorine molecules.

In essence, since the laser intensity required for a five-photon process is substantial, the outermost electron of the molecule starts wiggling with the laser field. As a result, the molecular potential and the dissociation threshold are shifted by a similar amount as the two atoms separate from each other, as shown by the dashed curves in Fig. 1. The total kinetic energy of the dissociation fragments at the point of creation is shifted and is given by

$$E_{\rm kin} = n\hbar\omega - (E_{^4P} + D_0^0) - U^e_{\rm ac} , \qquad (1)$$

where D_0^0 is the ground-state dissociation energy of Cl$_2$, $E_{^4P}$ is the energy of the ^4P Cl atom, $U^e_{\rm ac}$ is the ac-Stark shift of the electron in the ^4P Cl atom, and n is the number of photons needed to populate the dissociative molecular state ($3^3\Pi_u$ for our case). Here we assume that the wiggling of the nuclei is negligible. Note that the mechanism presented here for chlorine can be generalized for any case. As shown in Fig. 1, the neutral $3^3\Pi_u$ and ionic $X^2\Pi_g$ states have been shifted by $U^e_{\rm ac}$ and by the ponderomotive potential U^e_p, respectively. Once the molecule dissociates and the atoms start to absorb more photons, the situation becomes completely different from one in which the excitation is from an unshifted ground state. For excited atoms which are formed in intense fields, the photoelectron kinetic energy at the point of creation is

$$E_{{\rm kin},e} = m\hbar\omega - ({\rm IP} - E_{^4P}) + U^e_{\rm ac} - U^e_p , \qquad (2)$$

where m is the number of photons required to ionize the excited fragments (note $m \ll n$). If we assume that both initial and final states have shifted by the same amount ($U^e_{\rm ac} = U^e_p$), the situation will be exactly the same as the field-free ionization where the electron kinetic energy is $E_{{\rm kin},e} = m\hbar\omega - ({\rm IP} - E_{^4P})$. Thus, the electron kinetic energy at creation is *independent* of the laser intensity. This is also the measured kinetic energy when the laser pulse width is in the short-pulse regime. However, in our long-pulse experiment, the measured kinetic energy will be

$$E^{\rm det}_{{\rm kin},e} = m\hbar\omega - ({\rm IP} - E_{^4P}) + U^e_{\rm ac} , \qquad (3)$$

which is increased by the amount $U^e_{\rm ac}$ and is *intensity dependent.* Furthermore, the increase (decrease) in the kinetic energy of the electron (Cl fragment) is a direct measure of the ac-Stark shift of the excited state. Figure 3 shows the measured kinetic energy shifts for electrons (open circles) and ^4P Cl atoms (solid circles) as a function of laser intensity for 527 nm radiation. Note that the electron and atomic fragment shifts are equal in magnitude but opposite in sign, consistent with Eqs. (1) and (3). The solid line indicates the detected kinetic energy assuming a pure ponderomotive shift U^e_p and the dashed line is the calculated ac-Stark shift of the ^4P state using single-channel quantum-defect theory (SQDT). The large ac-Stark shift for the ^4P_J state, which is approximately equal to U^e_p, is due to the strong couplings at these frequencies to the $4p$ states. Note that the measured shifts are linear with laser intensity and thus consistent with the lowest-order perturbation theory scaling.

The physical process proceeds as follows: Ground-state Cl$_2$ is promoted to a superexcited state [Cl$_2$]* via five-photon absorption with its outer electron wiggling proportional to the field. The [Cl$_2$]* can autoionize or dissociate. Dynamically, as the two atoms separate, the wiggling electron finds itself on the excited ^4P atomic fragment. Thus, the additional electron energy $U^e_{\rm ac}$ results in a loss in the fragments' kinetic energy of an equal amount. Subsequent ionization of the ^4P fragment proceeds in an unperturbed (field-free) manner since the field energy $U^e_{\rm ac}$ is already incorporated into the ^4P electron. Some immediate consequences of this scenario are as follows. (1) Information concerning the field-atom interaction can be extracted from the kinetic energy analysis of either fragment (ground or excited) at any time after the intense pulse, regardless of the pulse's temporal regime [Eq. (1) is always valid]. (2) Interpretation of this model predicts an ability to suppress lowest-order dissociation channels in a manner directly analogous to suppression of ionization. Even more subtle is the capability to dramatically alter the dissociation cross section via dynamical shifts of repulsive potentials.

Another consistent observation involving the atoms excited to the ^4P_J states which supports the argument that these atoms are indeed formed in the presence of intense fields is the measured ATI yield in this experiment. Observation of ATI for a low-order process (two photons) is generally unlikely under standard experimental conditions where isolated atoms are allowed to experience rising laser intensities (low field saturation). For example, in the three-photon nonresonant ionization of Ca with 532 nm [7], the maximum amount of ATI observed was about 0.5%. On the contrary, the electron signal present in the ATI peaks of the ^4P_J state shown in Fig. 2 is over 18% at $I=5\times10^{12}$ W/cm^2. This high ATI yield became possible only because the ^4P Cl have been prepared in an intense field via a highly nonlinear dissociation. Thus, the saturation intensity is determined by the five-photon absorption of the molecule, *not* the low-order atomic ionization. To further substantiate our model we have calculated the cross sections for two- and three-photon ionization of the ^4P state using SQDT, yielding $\sigma_2=1.54\times10^{-49}$ cm^4/sec and $\sigma_3=2.14\times10^{-81}$ cm^6/sec^2. Using these cross sections in simple rate equations we obtained the ATI ratio, $R_3/R_2=0.2$ at $I=5\times10^{12}$ W/cm^2, which is in good agreement with our measured ratios. It is important to note that the quantum defects of the singly excited states which we employed in the calculation do not show significant anomalies. Thus, one might expect that SQDT would be adequate for this study.

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[1] For example, *Multiphoton Processes,* Proceedings of the Fifth International Conference on Multiphoton Processes, Paris, 1990, edited by G. Mainfray and P. Agostini (CEA, Gif-sur-Yvette, 1991).

[2] R. Freeman, P. Bucksbaum, H. Milchberg, S. Darack, D. Schumacher, and M. Geusic, Phys. Rev. Lett. **59**, 1092 (1987).

[3] T. W. B. Kibble, Phys. Rev. Lett. **16**, 1054 (1966); P. Bucksbaum, M. Bashkansky, and T. McIlrath, Phys. Rev. Lett. **58**, 349 (1987).

[4] See, for example, B. Yang, M. Saeed, L. F. DiMauro, A. Zavriyev, and P. Bucksbaum, Phys. Rev. A **44**, R1458 (1991), and references therein.

[5] P. Lambropoulos, Phys. Rev. Lett. **55**, 2141 (1985).

[6] R. R. Jones and P. H. Bucksbaum, Phys. Rev. Lett. **67**, 3215 (1991); H. Stapelfeldt, D. G. Papaioannou, L. D. Noordam, and T. F. Gallagher, Phys. Rev. Lett. **67**, 3223 (1991).

[7] L. F. DiMauro, D. Kim, M. W. Courtney, and M. Anselment, Phys. Rev. A **38**, 2338 (1988).

[8] M. Saeed, D. Kim, and L. F. DiMauro, Appl. Opt. **29**, 1752 (1990).

[9] B. Koenders, S. Koeckhoven, G. Kuik, K. Drabe, and C. de Lange, J. Chem. Phys. **91**, 6042 (1989); S. D. Peyerimhoff and R. J. Buenker, Chem. Phys. **57**, 279 (1981).