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Control of Branching Ratios in the Dissociative Ionization of Deuterium Chloride

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The dissociative ionization of deuterium chloride (DCl) has been investigated by employing femtosecond laser pulses at 805 nm. The product branching ratio D^+/Cl^+ of the fragments D^+ and Cl^+ is strongly affected by the chirp α of the laser pulses. The ratio can be controlled by a factor of 3 ranging from $D^+/Cl^+ = 0.7$ at $\alpha = -800$ fs^2 to $D^+/Cl^+ = 1.9$ at $\alpha = +150$ fs^2. The observation can be rationalized by a model where negative chirp favors intra-electronic state excitation, and positive chirp favors inter-electronic state excitation in the dissociation of the molecular ion. Complementary experiments on hydrogen chloride (HCl) are discussed.

1. Introduction

Attempts to control elementary photophysical and photochemical processes have received considerable interest in recent years. Examples are the photoionization/photodissociation,[1−7] polarization,[8−10] high-order harmonic generation[11,12] and photoassociation[13−16] of molecules. One common aspect is connected to the phase relation of intermediate wave functions,[17,18] which constitutes a key to coherent control schemes.

In general, the control of photochemical processes appears feasible by variation of the laser wavelength, intensity, pulse duration or the chirp. In particular, the chirp of broadband femtosecond laser pulses has provided valuable insight, last but not least due to the technical progress in manipulating the time dependence of the laser frequency, e.g., by liquid-crystal displays (LCD)[19] and deformable mirrors.[20,21] Consequently, chirped femtosecond-laser pulses have been used to induce, e.g., ladder climbing in anharmonic molecular potentials,[22,23] as suggested by Chelkowski et al.[24]

The influence of chirp on the product yields in the dissociative ionization of methane has been investigated by Mathur and Rajgara[4] at 800 nm with intensities ranging from 10^{15} to 10^{16} W/cm^2. Besides from the parent ion the most intense ion signals were observed for H^+ and CH_3^+. Mathur et al. showed that the ratio of H^+ to CH_3^+ depends on the chirp of the femtosecond-laser pulses, with positive chirp (frequency increasing with time) slightly favoring the H^+ channel. Yamanouchi and co-workers [5] studied the dissociative ionization of ethanol at 800 nm with intensity up to 4×10^{15} W/cm^2. Chirped laser pulses have been found to induce more fragmentation than transform limited pulses; however, the relative yields were not affected by the sign of the chirp within the error limits—in contrast to the methane experiments. From the literature it is thus not clear under which conditions an influence of chirp on dissociative ionization can be expected, suggesting that further investigation is required. For mid-IR excitation Corkum et al. described the dissociative ionization of H_2.[25] Predominantly, dissociation appeared to occur in the ion.

In the current work we have investigated the influence of a linear chirp on the ratio of fragment ion yields in the dissociative ionization of deuterium chloride (hydrogen chloride). The ionization/dissociation of DCl (HCl) molecules has received particular attention in recent years both from experimental[26] and from theoretical[17,27,28] points of view. According to theoretical estimates by Paci et al.,[28] sequential ionization of neutral HCl followed by dissociation of the ion should dominate for intensities between 10^{13} and 10^{15} W/cm^2. Both dissociation of neutral HCl and sequential double ionization are expected to be operative only at even higher intensities. Consequently, the dissociative ionization of HCl investigated by Corkum and co-workers most likely corresponded to sequential ionization followed by dissociation.[27] In that work the intensity dependence of fragment ion formation was investigated. In the current work we have investigated the chirp dependence of branching ratios in the dissociative ionization of DCl molecules around 800 nm for similar intensities.

2. Method

The dissociative ionization of DCl molecules has been investigated in a homemade linear time-of-flight mass spectrometer (TOF-MS). The TOF-MS consists of a double-stage acceleration and a 30 cm field-free drift tube combined with a tandem microchannel plate detector. Very high collection efficiency is ensured by operating the ion source at a field of 300 V/cm, preventing at the same time discrimination of ions. The ionizing radiation is generated in a femtosecond-laser system consisting of a 20 fs Ti:sapphire oscillator (Femtosource Compact, Femtolasers Inc.) seeding a multipass amplifier (Odin, Quantronix Inc.). The amplifier delivers 1 kHz laser pulses at 805 nm (bandwidth ca. 40 nm) with pulse energy up to 1.2 mJ. The pulse duration can be adjusted in a range between about 45 and 200 fs, e.g., by adjusting the compressor length of the amplifier. This does not affect the pulse energy. The pulse duration τ is measured by an autocorrelator (Pulse Check, APE Inc.). Assuming Gaussian pulses it is directly correlated to the linear chirp parameter α measured in fs^2 by eq 1.[29] The predominance of linear chirp has been confirmed by FROG

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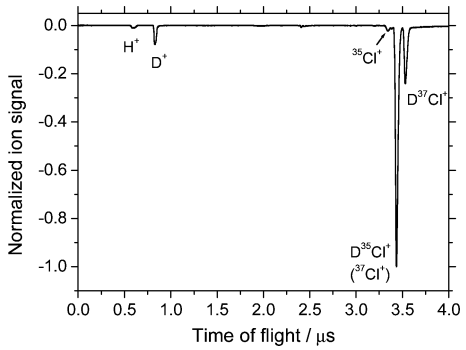

Figure 1. Overview TOF-MS of deuterium chloride. Estimated laser intensity 9×10^{13} W/cm^2, pulse width 45 fs (near transform limited), $\lambda = 805$ nm.

measurements (GRENOUILLE, Newport Inc.). The chirp, in particular its sign, is calibrated by introducing optical material of known group velocity dispersion into the light path. The laser pulses with the shortest autocorrelation times τ_o are assumed to be nearly transform limited, i.e., chirp free.

$$\tau^2 = \tau_o^{\,2} + (8\alpha \ln 2/\tau_o)^2 \qquad (1)$$

The chirp can be directly translated into the time dependence of the laser frequency by

$$\omega(t) = \omega_o + \frac{\alpha\left(\frac{\Delta\omega^2}{\ln 2}\right)^2 t}{8 + 2\alpha^2\left(\frac{\Delta\omega^2}{\ln 2}\right)^2} \qquad (2)$$

The laser radiation is focused into a vacuum chamber, which contains the sample, by an $f = 250$ mm aluminum mirror. Most of the experiments shown in this work have been obtained at a laser power of 0.5 mJ/pulse (sections 3.1 and 3.2). Assuming classical optics for the airy disk, we estimate a maximum intensity for the case of unchirped pulses of 9.2×10^{13} W/cm^2. Complementary experiments at higher or lower laser power have also been performed (section 3.3). All autocorrelation measurements are performed outside the vacuum chamber, however, under conditions directly equivalent to the ion source. The influence of the quartz windows has been taken into account from known dispersion data.[30] The laser light is linearly polarized, with the plane oriented perpendicular to the spectrometer axis unless otherwise noted.

TOF spectra are recorded by typically averaging over 1000 laser shots. The sample has been introduced into the vacuum chamber under thermal conditions. DCl has been purchased from Sigma Aldrich, deuterium purity was specified at 99%.

3. Results and Discussion

3.1. TOF Mass Spectra. Typical TOF mass spectra obtained in this work (see Figure 1) exhibit the parent ions $D^{35}Cl^+$ and $D^{37}Cl^+$ (respectively, $H^{35}Cl^+$ and $H^{37}Cl^+$), and the fragment ions D^+ and $^{35}Cl^+$. The fragment ion $^{37}Cl^+$ coincides with the $D^{35}Cl^+$ peak and is hidden underneath the latter. The natural abundance of the two Cl isotopes is well-known (75:25). Since there is no indication of isotope selectivity in the current experiments, the contribution of different isotopes is easily taken into account in the analysis. Note that multiply charged species are not observed at significant levels. The H^+ ion signal observed in Figure 1 in part originates from hydrogen chloride present in the sample at a 1% level. Part of this signal may also be due to other impurities in the chamber.

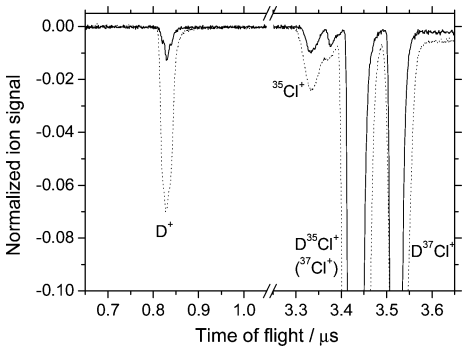

Figure 2. TOF-MS spectra of DCl recorded for chirp +725 fs^2 (dots) and −730 fs^2 (solid). Spectra are normalized to the parent ion yield.

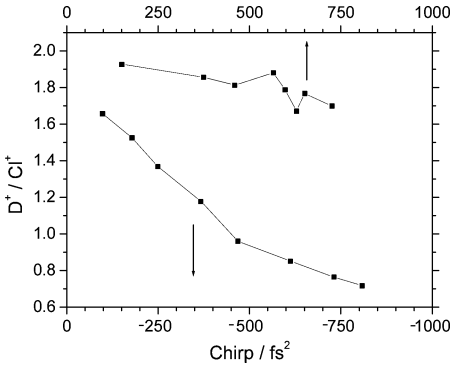

Figure 3. Chirp dependence of the product branching ratio D^+/Cl^+. Both Cl^+ isotopes have been taken into account. Lines through data points are to guide the eye. Estimated reproducibility is ±0.05.

The TOF-MS spectra for the dissociative ionization of DCl exhibit pronounced polarization effects, which have been discussed elsewhere.[31] In particular, from experiments with parallel polarization (laser field relative to spectrometer axis) we see clear evidence for anisotropy of the dissociative ionization. Only at the highest fluence is discrimination of D^+ ions with very high kinetic energy observed for perpendicular polarization. This reduces the effect of multiply charged parent ions that tentatively lead to fragment ions (in particular, D^+) with very high kinetic energy. All data shown here have been obtained for perpendicular polarization.

3.2. Influence of the Chirp. In the following we discuss the influence of a linear chirp on the TOF mass spectra. For illustration, Figure 2 shows TOF spectra for two different chirp values of +725 (dots) and −730 fs^2 (line). The absolute chirp values of the data sets being almost identical (the difference is only in the sign) implies that the pulse intensity distributions are also almost identical. Evidently, the ratio of D^+ and Cl^+ ion yields strongly depends on the sign of the chirp. The effect is significantly larger for the D^+ ion compared to the Cl^+ ion, i.e., the change in the D^+ ion yield is much more pronounced than that of the Cl^+ ion yield. Evidently, a positive chirp favors the formation of D^+ much more than a comparable negative chirp does. The peak at 3.38 μs originates from $H^{35}Cl^+$ present in the sample at a fraction of 1% from the production process. The width of all ion signals is apparently larger for the TOF-MS with up-chirp, due to the slightly higher signal level for these conditions. This width and the apparatus function do not affect the fragmentation.

In the following we discuss the ratio of fragment ion yields D^+/Cl^+, where both chlorine isotopes ($^{35}Cl^+$ and $^{37}Cl^+$) have been taken into account. Figure 3 shows this ratio for a systematic variation of the linear chirp. The smallest product ratio $D^+/Cl^+ = 0.7$ is observed for a negative chirp of about

−800 fs^2. With increasing value of the chirp (less negative) the product ratio also increases. The largest ratio occurs for a slightly positive chirp of +150 fs^2. However, variation of the chirp from +150 to about +750 fs^2 has only a modest effect on the branching ratio. Note that data points in Figure 3 connected by a vertical line correspond to experiments that differ only in the sign of the chirp. Because for such a comparison both pulse energies and autocorrelation times are identical, this implies that the pulse intensity distributions are also almost identical. We have performed additional experiments on the dissociative ionization of HCl. For HCl the ratio of H^+/Cl^+ ion yields increases again with increasing chirp. The common characteristics are that for a given absolute chirp value the product branching ratio H^+/Cl^+ with respect to D^+/Cl^+ is larger for positive chirp than for negative chirp.

3.3. Influence of the Intensity. Additional experiments have been performed at significantly higher laser pulse energies up to 1.2 mJ/pulse. As a general trend, the amount of fragmentation increases with increasing pulse energy. At the same time the extent of multiple charging also increases. The data on the chirp effect described in section 3.2 have been observed under conditions where double ionization of molecules can be safely excluded. In principle, any fragment ion could also originate from sequential fragmentation/ionization, i.e., the process DCl + $h\nu \rightarrow$ D + Cl followed by ionization of one of the fragments. However, the latter would require that fragmentation effectively takes place on the time scale of the laser pulse. Given the relatively short pulse durations down to 45 fs this seems highly unlikely. Both conclusions are in line with estimates by Paci et al.[28] In addition, we note qualitatively the same trend of the chirp dependence for pulse energies between 0.2 and 1.2 mJ for both polarization planes, although the absolute numbers differ. At pulse energies below 0.2 mJ fragmentation yields become too small to be measured accurately.

4. Discussion and Summary

We have investigated the dissociative ionization of deuterium chloride (hydrogen chloride) by employing femtosecond pulses at 805 nm for a range of laser powers as a function of the linear chirp of the laser pulses. For all laser powers a significant influence of the sign of the chirp on the product branching ratio D^+/Cl^+ is observed. For a pulse energy of 0.5 mJ/pulse the product ratio varies over almost a factor of 3 in the range of linear chirp between −800 and +800 fs^2.

Chirping a femtosecond-laser pulse is in general accompanied by an increase in the effective pulse duration, thus a decrease in intensity. In fact, it is often impossible to distinguish pure chirp effects from intensity effects. The main advantage of the current work is connected to the ability to study both positive and negative chirp over a wide range. Looking only at a variation of, e.g., positive chirp values would make the distinction of chirp and intensity effect almost impossible. Because we are able to perform experiments under essentially identical intensity conditions, the only difference being the sign of the chirp, we are unambiguously able to proof the effect of chirp. The factor of 3 increase of the product branching ratio discussed above is, thus, exclusively due to the difference in chirp. The same trend of increasing product branching ratio with increasing chirp is observed for both isotopomers DCl and HCl.

Few other experiments describing systematic variation of chirp effects in the dissociative ionization of molecules are currently available. In the dissociative ionization of methane it was observed that a positive chirp favors the ratio of H^+ to CH_3^+.[4] Possibly this trend is connected to the heat of formation of the relevant fragments. Apparently the energetic upper channel (H^+) is favored by up-chirp. On the other hand, no influence of the sign of the chirp has been found in the dissociative ionization of ethanol[5] and in the dissociation of H_2^+ ions.[32] The results reported in the current work show the same trend as Mathur's work, in that positive chirp also favors the D^+ (H^+) channel. Although there is strong evidence of sequential ionization followed by dissociation of the ion in the current experiment, the question remains in which state the influence of the chirp takes place.

Assuming that the chirp affects the ion dissociation, the results can be rationalized by assuming that down-chirp favors excitation within the ion ground state (intra-electronic state excitation) leading to the formation of Cl^+, and up-chirp favors eventual excitation to a higher electronic state (inter-electronic state excitation) leading to the formation of D^+. This would be considered most likely for mid-IR excitation, perhaps less likely for the current excitation at 805 nm, where nominally only 3−4 photons are required for dissociation of the ion. On the other hand, we have previously demonstrated that the observed branching ratio D^+/Cl^+ is the result of a complex interplay of wavelength, intensity and chirp.[17] For the future we plan to extend our wave packet calculations to the 800 nm regime and to laser fields of the strength available to our experiment.

It is also interesting to note that the Keldysh parameter[33] γ is larger than 1 for all of our experiments, indicating that we are in the multiphoton regime rather than the tunneling regime. However, we cannot exclude the possibility that the internal energy of the intermediate ions differs for different signs of the chirp. Clearly, more experiments are needed to resolve these questions.

5. Outlook

Dissociative ionization plays a key role in many control schemes. Because, in general, excitation and ionization pathways compete with fragmentation pathways, it seems rewarding to perform additional experiments in the future where part of these pathways can be excluded. One possible experiment could be a two-color experiment where parent ions are formed by a first femtosecond-laser pulse and the fragmentation of these primary ions is induced by a second laser pulse. Such an experiment is currently underway in our laboratory.

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