JOURNAL OF CHEMICAL PHYSICS VOLUME 108, NUMBER 11 15 MARCH 1998

Quantum control of the yield of a chemical reaction

Igor Pastirk, Emily J. Brown, Qingguo Zhang, and Marcos Dantus[a)]
Department of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan 48824

(Received 4 December 1997; accepted 9 January 1998)

Order of magnitude enhancement in the concerted elimination pathway leading to I_2 product formation in the photodissociation reaction of CH_2I_2 by the use of positively chirped 312 nm femtosecond laser pulses is demonstrated. The maximum yield is found for chirps of 2400 fs^2 while the minimum is found near -500 fs^2. Multiphoton excitation with 624 nm pulses results in the opposite effect, where the maximum yield is found near -500 fs^2. The enhancement as a function of chirp is found to depend on the wavelength and intensity of the laser pulses. These results offer new experimental evidence for quantum control of chemical reactions. © *1998 American Institute of Physics.* [S0021-9606(98)02711-1]

The goal for active laser control is to devise electromagnetic fields that drive the outcome of a chemical reaction in the desired direction.[1] There are basically two approaches to this problem. The frequency-resolved scheme (also known as coherent control), proposed by Brumer and Shapiro,[2] utilizes quantum interference between different pathways to a final state to exert control over the outcome. One of the most striking demonstrations of this scheme is found in the work of Gordon and co-workers where they control autoionization versus predissociation in HI and DI molecules.[3] The time-resolved scheme (also known as pump dump), proposed by Tannor and Rice,[4] exploits the time-dependent motion of wave packets created by ultrafast (usually femtosecond) laser pulses to manipulate the outcome of the reaction. Experimental demonstrations of this control scheme are found in many pump–probe time-resolved experiments, e.g., the excitation of I_2 to produce either the $D(^1\Sigma_u^+)$ or the $F(^1\Sigma_u^+)$ states,[5] or the production of Na^+ or Na^{2+} as a function of time delay between pump and probe pulses.[6] The application of chirped pulses to shape nuclear wave packets and enhance vibrational coherence was proposed by Ruhman and Kosloff.[7] the search for an optimal electromagnetic field in terms of spectral and temporal composition to control the outcome of a chemical reaction was first formalized by Rabitz.[8] Wilson, Mukamel, and co-workers generalized this analysis to obtain a formalism which is more amenable for the study of thermal ensembles of molecules.[9] Optimization of the Tannor–Rice pump-dump scheme for controlling the selectivity of produce formation was considered by Kosloff *et al.*[10] Boers *et al.* demonstrated the use of chirped pulses to enhance the population transfer in the three-state ladder, $5s \rightarrow 5s \rightarrow 5p \rightarrow 5d$, of the rubidium atom.[11] Experimental[12] and theoretical[13] studies on the effect of chirped pulses on the multiphoton excitation of molecules showed that the traditional saturation limits can be exceeded, thereby facilitating population inversion. The groups of Shank, Wilson, Gerber, and Leone have recently shown experimental evidence that tailored femtosecond pulses can be used to modify the initial wave packet formed by the excitation laser[14] and, in some cases, tailored pulses can be used to enhance single and multiphoton excitation.[15] The results presented in this communication provide evidence to the effect of chirp on the yield of a photodissociation pathway for polyatomic molecules.

The product state (i.e., electronic, vibrational, rotational, and translational) distribution resulting from the photodissociation of polyatomic molecules depends upon the potential energy surfaces participating in the fragmentation process, along with their couplings and the characteristics of the incident electromagnetic field.[16] The field is characterized by its frequency, duration, intensity, and chirp. Chirp is naturally caused by the propagation of laser pulses through matter which leads to group velocity variations as a function of frequency within the pulse, thus causing a frequency sweep.[17] In most cases the group velocity variation causes a positive chirp in which the leading edge of the pulse is redshifted and the trailing edge is blueshifted with respect to the central frequency of the pulse. Negative chirp corresponds to the opposite effect. Increases in absolute chirp lead to a temporal broadening of the pulse and are usually considered detrimental for the study of ultrafast phenomena, where the best time resolution is required. Recently, chirp has been recognized as an important parameter that can be used to control the dynamics of a system excited by ultrafast laser pulses.[7,11–15]

The shape and time evolution of a quantum mechanical wave packet $\psi(t)$ produced through absorption of an ultrafast laser pulse are determined, in part, by the phase factors in the following expression:

$$\psi(t) = \sum_n a_n e^{-iE_n t/\hbar} \varphi_n , \tag{1}$$

where E_n and φ_n denote the eigenvalue and eigenfunctions of each level n. The quantity a_n is given by the Franck–Condon overlap between the initial and each final state n. The initial phase factor for each eigenstate, the quantity in the exponential, is equal for all states when excitation takes

---

[a] Electronic mail: dantus@cem.msu.edu

© 1998 American Institute of Physics

place with transform limited pulses, i.e., no chirp. However, chirped pulse excitation opens the possibility for introducing different initial phases. Therefore, the shape and dynamics of the wave packet can be controlled by chirped pulses with the goal of affecting the outcome of a chemical process.[7,14,15]

The following experiments were carried out with a homebuilt femtosecond laser system consisting of a colliding pulse mode-locked dye laser (CPM) pumped by an Ar^+ laser. The CPM output was amplified in a pulsed dye amplifier. The amplified pulses were compressed by a two-prism, double-pass pulse compressor. The laser system produced pulses with 47 fs temporal width and with the central wavelength at 624 nm. Typical pulse energy was 0.4 mJ (30 Hz repetition rate), but was attenuated for the experiments to 70 μJ. In cases where 312 nm femtosecond pulses were necessary, the 624 nm beam was frequency doubled by a KDP crystal (0.1 mm) producing $\sim$7 μJ pulses. The pulses were then focused into a quartz cell containing the gaseous sample. Fluorescence signals originating from the cell were collected along the direction perpendicular to the laser beam propagation through a 0.27 m spectrometer. The laser intensity of the 312 nm beam was continuously monitored by a photodiode.

One of the compression prisms was mounted on a computer-controlled actuator. Translation of the prism along its bisector varied the amount of glass through which the beam propagated and permitted the introduction of linear chirp. Because the amount of chirp was computer controlled, scans of signal intensity as a function of chirp could be achieved in a convenient and fast manner. Characterization of the femtosecond pulses was carried out by frequency resolved optical gating (FROG).[18] FROG measurements in our laboratory provided direct measurements of the frequency components of each pulse as a function of time, from which the linear chirp was determined. A continuous chirp scale as a function of prism position was compiled using the expression for group velocity dispersion as a function of prism position derived by Fork *et al.*[19] and simplified by Salin and Brun.[20]

Quartz cells containing iodine, I_2, or methylene iodide, CH_2I_2 (Aldrich 99%), were prepared on a vacuum line, and were degassed to less than 10^{-6} Torr. Iodine scavenging agents (sodium thiosulphate and copper) were introduced in the CH_2I_2 cell to ensure that the signal derived only from nascent iodine. Experiments were carried out at room temperature (21 °C) with vapor pressures of 0.25 and 1.2 Torr for I_2 and CH_2I_2, respectively.

Spectral profiles for the 624 and 312 nm pulses measured at zero, negative, and positive chirps were obtained in order to experimentally confirm that the introduced chirp did not affect the spectrum of the pulses. The intensity variations of the 624 and 312 nm pulses as a function of chirp were also measured. The intensity of the fundamental remained essentially constant; whereas, a small variation in the UV intensity was observed. This variation can be understood in terms of the dependence of second-harmonic generation on the peak intensity of the incoming pulses. As absolute chirp increases, the pulse width increases resulting in a reduction of peak intensity.

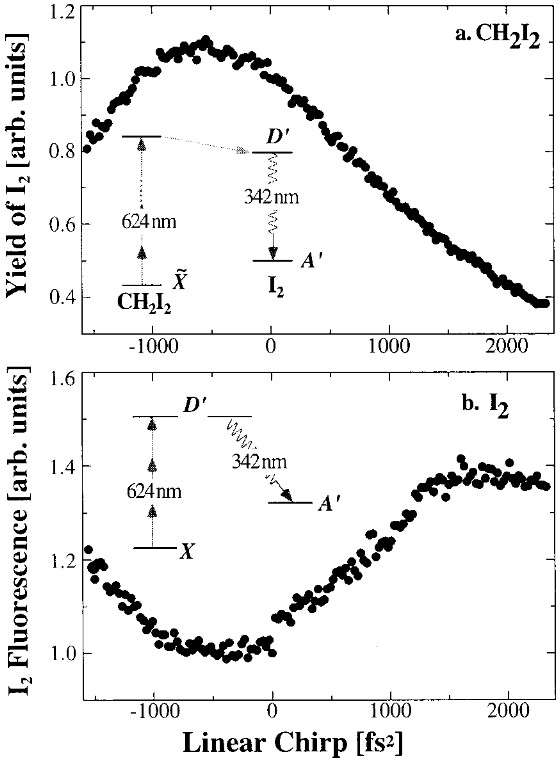

FIG. 1. (a) Experimental measurement of the yield of the molecular pathway producing I_2 from the multiphoton dissociation of CH_2I_2 with 624 nm laser pulses as a function of chirp. The insert shows the relevant energetics for the reaction. (b) Same as (a) except for I_2.

The concerted elimination of I_2 molecules following irradiation of CH_2I_2 is known to occur for excitation energies larger than $\sim$9.4 eV.[21] The yield of this molecular process has been measured to be on the order of 1%. Most other pathways, produce atomic iodine in its ground (I) and spin–orbit excited states (I*). The nascent I_2 molecules are formed primarily in the D' state and have been detected following single and multiphoton excitation.[22] In our laboratory, we have explored the femtosecond dynamics of the molecular detachment process and have found it to take place in less than 50 fs.[23] We have also found that other halogenated alkanes with formulas CX_2Y_2 for (X=H, D, F and Y=Cl, Br, and I) undergo similar molecular detachment processes.[24] Detection of the molecular product is selectively carried out by dispersing the laser-induced fluorescence and collecting only a spectral window that contains the majority of the $D' \rightarrow A'$ emission.

Multiphoton excitation of CH_2I_2 with 624 nm pulses produces the well-known I_2 $D' \rightarrow A'$ emission at 342 nm. Figure 1(a) presents variations in the relative yield of the molecular detachment pathway as a function of linear chirp. The data have been normalized to unity at zero chirp. Note that the maximum yield is observed for -500 fs^2 and the minimum at 2400 fs^2. We observe a factor of 2.9 in the overall change in the yield for this pathway as a function of chirp. These data are contrasted with a chirp scan obtained under similar conditions with the 624 nm pulses on the yield from three-photon excitation of I_2 vapor to yield $D \rightarrow X$ and $D' \rightarrow A'$ fluorescence between 320 and 345 nm. These re-

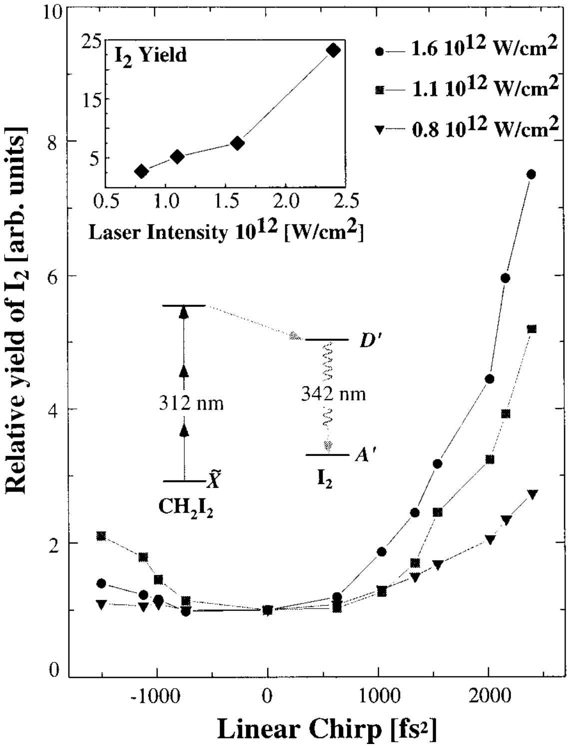

FIG. 2. Experimental measurement of the yield of the molecular pathway producing I_2 from the multiphoton dissociation of CH_2I_2 with 312 nm laser pulses as a function of chirp. The inserts show the relevant energetics for the reaction as well as a plot of the maximum I_2 yield enhancement recorded at 2400 fs^2 chirp as a function of laser peak intensity (measured at zero chirp).

sults are presented in Fig. 1(b) and show an opposite trend to that obtained for CH_2I_2 dissociation. The minimum yield for the three-photon excitation is found at -500 fs^2 but increases by ~40% as the magnitude of chirp increases. Wilson and co-workers have investigated the chirp effect on the three-photon absorption yield for I_2 at 550, 570, and 600 nm.[15] They found the yields are significantly affected by the chirp (approximately factors of 2 and 3 for 600 and 570 nm excitation, respectively). Our results on I_2 are in very good agreement with their findings.

We have also explored the effect of chirp on the multiphoton excitation of CH_2I_2 with 312 nm laser pulses. Figure 2 presents the yield of the molecular pathway determined by detection of I_2 $D' \rightarrow A'$ fluorescence intensity as a function of chirp. For these experiments, both the fluorescence signal and 312 nm laser intensity were recorded and averaged for 500 laser shots at each chirp stop. The fluorescence intensity was normalized against the third power of the 312 nm intensity (because of the three-photon excitation and the inherent variation of 312 nm intensity as a function of chirp *vide supra*). It is clear that increasing the chirp enhances the photodissociation yield significantly.

The molecular pathway enhancement is found to be nonsymmetric, favoring positive over negative chirps. This observation implies that the observed enhancements are not due to pulse width effects but rather depend on the magnitude and sign of the linear chirp. The three scans shown in Fig. 2 were obtained under identical conditions except for the intentional changes in the pulse intensity from 0.8 to 1.6 $\times 10^{12}$ W/cm^2 (calculated for zero chirp pulses). The data are shown normalized to laser pulse energy but are not corrected for variations in peak intensity caused by pulse broadening as a function of chirp. The effect of laser intensity on these control experiments is shown in the insert, where the molecular pathway yield is shown to increase for positive 2400 fs^2 chirp by factors of 3–25 as the zero-chirp intensity of the laser pulses in increased from 0.8 to 2.4×10^{12} W/cm^2, see Fig. 2 insert.

We consider the differences between the dependence of the molecular pathway yield on laser pulse chirp for 624 and 312 nm excitation to be of great interest. For 624 nm, the yield decreases with absolute chirp, while for 312 nm it increases. We have not taken into account the fact that the temporal pulse width of the pulses increases with linear chirp. Multiphoton transitions are, in general, expected to increase by factors proportional to the peak intensity raised to the nth power (I^n) where n is the number of photons. Therefore, multiphoton excitation is expected to be maximized when the chirp is zero. For 624 nm excitation, the maximum yield was found for a chirp of -500 fs^2; however, for 312 nm the maximum yield was found for a chirp of 2400 fs^2. Based on the pulse width change and the three-photon excitation for the 312 nm case, the transition probability, proportional to ($I^{n=3}$), is expected to decrease by a factor of 27 (because the pulse width triples at this chirp value). Therefore, the yield of I_2 production should track with the transition probability instead of showing the observed enhancement.

The effects caused by chirp in the excitation pulses reflect characteristics of the potential energy surfaces and the nascent wave packet dynamics. For diatomic I_2, Wilson and co-workers have been able to explain their observed chirp effects based on quantum mechanical calculations that show a ''wave packet following'' effect for positive chirp.[5] Currently, the potential energy surfaces involved for CH_2I_2, are not known preventing us from giving an accurate quantum mechanical description of the effect. In principle, a similar wave packet following effect could be responsible given that the first photon transition is resonant, as in the I_2 experiment from Wilson's group.[15] The order of magnitude changes demonstrated in this communication give additional evidence that quantum control of the yield of chemical reactions involving polyatomic molecules is a promising area of research.

In summary, we have found that the chirp of femtosecond pulses can have profound effects on the photophysical and photochemical processes. For diatomic iodine, both positive and negative chirps enhanced I_2 fluorescence signals. These findings are in good agreement with those obtained by Wilson and co-workers.[15] However, for the multiphoton photodissociation of CH_2I_2 with 624 nm, the opposite chirping effects with the maximum I_2 yield near chirp zero is observed. Results for 312 nm multiphoton excitation of CH_2I_2 exhibit a minimum I_2 yield near chirp zero. The yield of the molecular pathway is found to be asymmetric with respect to the sign of the chirp and enhancements up to a factor of 25 for positive chirps are observed. The amount of enhancement is also found to be highly dependent on the pulse intensities.

Future experiments will further probe this observation.

This research was partially funded by a Camille and Henry Dreyfus New Faculty Award. M.D. is an Arnold and Mabel Beckman Young Investigator and a Lucille and David Packard Science and Engineering Fellow. We want to thank the Wilson group for providing us with a preprint of their work. E.J.B. is supported by a National Science Foundation Graduate Fellowship.

[1] See, e.g., R. J. Gordon and S. A. Rice, Annu. Rev. Phys. Chem. **48**, 601 (1997); P. Brumer and M. Shapiro, Acc. Chem. Res. **22**, 407 (1989); M. Shapiro and P. Brumer, J. Chem. Phys. **98**, 201 (1993); S. Shi and H. Rabitz, *ibid.* **92**, 364 (1990).

[2] M. Shapiro and P. Brumer, J. Chem. Phys. **84**, 4103 (1986); P. Brumer and M. Shapiro, Annu. Rev. Phys. Chem. **43**, 257 (1992).

[3] L. Zhu, V. Kleiman, X. Li, S. Lu, and R. J. Gordon, Science **270**, 77 (1995); L. Zhu, K. Suto, J. A. Fiss, R. Wada, T. Seideman, and R. J. Gordon, Phys. Rev. Lett. **79**, 4108 (1997).

[4] D. J. Tannor, R. Kosloff, and S. A. Rice, J. Chem. Phys. **85**, 5805 (1986); D. J. Tannor and S. A. Rice, Adv. Chem. Phys. **70**, 441 (1988).

[5] R. M. Bowman, M. Dantus, and A. H. Zewail, Chem. Phys. Lett. **174**, 546 (1990).

[6] T. Baumert and G. Gerber, Isr. J. Chem. **34**, 103 (1994).

[7] S. Ruhman and R. Kosloff, J. Opt. Soc. Am. B **7**, 1748 (1990).

[8] S. Shi, A. Woody, and H. Rabitz, J. Chem. Phys. **88**, 6870 (1988).

[9] Y. J. Yan, R. E. Gillilan, R. M. Whitnell, K. R. Wilson, and S. Mukamel, J. Chem. Phys. **97**, 2320 (1993); J. L. Krause, R. M. Whitnell, K. R. Wilson, Y. J. Yan, and S. Mukamel, *ibid.* **99**, 6562 (1993).

[10] R. Kosloff, S. A. Rice, P. Gaspard, S. Tersigni, and D. J. Tannor, Chem. Phys. **139**, 201 (1989).

[11] B. Broers, H. B. van Linden van den Heuvell, and L. D. Noordam, Phys. Rev. Lett. **69**, 2062 (1992); and related theory Y. B. Band, Phys. Rev. A **50**, 5046 (1994).

[12] J. S. Melinger, A. Hariharan, S. R. Gandhi, and W. S. Warren, J. Chem. Phys. **95**, 2210 (1991).

[13] Y. B. Band and P. S. Julienne, J. Chem. Phys. **96**, 3339 (1992).

[14] C. J. Bardeen, Q. Wang, and C. V. Shank, Phys. Rev. Lett. **75**, 3410 (1995); C. J. Bardeen *et al.*, J. Phys. Chem. **A101**, 3815 (1997); B. Kohler *et al.*, Phys. Rev. Lett. **74**, 3360 (1995); C. J. Bardeen *et al.*, J. Chem. Phys. **106**, 8486 (1997); A. Assion, T. Baumert, J. Helbing, V. Seyfried, and G. Gerber, Chem. Phys. Lett. **259**, 488 (1996); J. M. Papanikolas, R. M. Williams, and S. R. Leone, J. Chem. Phys. **107**, 4172 (1997).

[15] V. Yakovlev, C. J. Bardeen, J. Che, J. Cao, and K. R. Wilson, J. Chem. Phys. (submitted); C. J. Bardeen, V. V. Yakovlev, K. R. Wilson, S. D. Carpenter, P. M. Weber, and W. S. Warren, Chem. Phys. Lett. (submitted).

[16] A. D. Hammerich, R. Kosloff, and M. A. Ratner, J. Chem. Phys. **97**, 6410 (1992).

[17] S. De Silvestri, P. Laporta, and O. Svetlo, IEEE J. Quantum Electron. **QE-20**, 533 (1984); E. B. Treacy, *ibid.* **5**, 454 (1969).

[18] R. Trebino and D. J. Kane, J. Opt. Soc. Am. A **10**, 1101 (1993).

[19] R. L. Fork, O. E. Martinez, and J. P. Gordon, Opt. Lett. **9**, 150 (1984).

[20] F. Salin and A. Brun, J. Appl. Phys. **61**, 4736 (1987).

[21] H. Okabe, M. Kawasaki, and Y. Tanaka, J. Chem. Phys. **73**, 6162 (1980).

[22] P. J. Dyne and D. W. G. Style, J. Chem. Soc. **1952**, 2122 (1952); D. W. G. Style and J. C. Ward, *ibid.* **1952**, 2125 (1952); C. Fotakis, M. Martin, and R. J. Donovan, J. Chem. Soc. Faraday Trans. **78**, 1363 (1982).

[23] U. Marvet and M. Dantus, in *Femtochemistry: The Lausanne Conference*, edited by M. Chergui (World Scientific, Singapore, 1996); Chem. Phys. Lett. **256**, 57 (1996).

[24] Q. Zhang, U. Marvet, and M. Dantus, J. Chem. Soc. Faraday Discuss. (in press).