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Multiple ionization of N_2 in intense, linearly and circularly polarized light fields

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There are significant differences in the multielectron dissociative ionization (MEDI) of N_2 by 100-fs-long laser pulses (intensity $10^{15}\,W\,cm^{-2}$) using linearly and circularly polarized light, with substantial suppression of ionization in the latter case. Enhanced ionization occurs in both instances at an internuclear distance *(r)* of ~2.2 Å, with an increased propensity for MEDI at larger *r* values with circularly polarized light. [S1050-2947(99)50107-8]

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Much progress has been made in recent years in gaining insights into a host of counterintuitive phenomena that arise in interactions of intense light fields with matter [such as above-threshold ionization (ATI) and dissociation, high harmonic generation (HHG), and stabilization [1]]. The strongly nonperturbative physics that governs such phenomena has made theoretical analysis difficult. Most of the effort has been on the application of one-dimensional numerical techniques directed towards investigations with linearly polarized light. Light of arbitrary polarization requires the use of at least two spatial dimensions. Some progress has been recently reported in studies of laser-atom interactions with light of arbitrary polarization [2]. In these theoretical studies circular polarization is shown to enhance ionization of a model atom at all but the lowest laser intensities ($<10^{13}$ $W\,cm^{-2}$ at 526 nm). On the other hand, in other studies of intense field atomic phenomena, circular polarization has usually been observed to result in the suppression of ionization (as in ATI) and of light emission (HHG) [3]. In atomic ionization that occurs in the low-intensity (perturbative) multiphoton regime, circular polarization can either enhance ionization (as in the case of Cs [4]) or suppress it [5].

The extension of such investigations to polarization-dependent molecular dynamics has hitherto remained virgin territory, and is the subject of the present study. Intense-field molecular dynamics with linearly and circularly polarized light is a subject that is both interesting and of importance because of the richness that is added by facets that are peculiar to molecules, such as enhanced ionization, competition between ionization and dissociation, bond softening/hardening, and spatial reorientation effects. It remains to be investigated how circular polarization affects the efficacy of existing one-dimensional models that predict phenomena such as enhanced ionization [6]. Furthermore, circularly polarized light *cannot* be merely treated as a combination of two perpendicular, linearly polarized components. In other words, the dynamics resulting from irradiation of molecules by circularly polarized light is not expected to be a linear combination of the dynamical effects due to linearly polarized light aligned parallel and perpendicular to the molecular symmetry axis. Moreover, circularly polarized light imparts angular momentum to the atom/molecule, whereas linearly polarized light does not. How this might affect molecular dynamics in intense laser fields is an issue that has not, to our knowledge, been addressed. We report here results of experiments on the multielectron dissociative ionization (MEDI) of a simple diatomic molecule, N_2, in intense, 100-fs-duration light fields (of intensity $10^{15}\,W\,cm^{-2}$, wavelength 806 nm) using coincidence time-of-flight (TOF) spectrometry. The morphology of our data reveals significant differences in the ionization dynamics using light that is linearly polarized and that obtained with circularly polarized light of the same intensity [7]. Care was taken to also make measurements with circularly polarized light at intensities that yielded the same electric field as in the case of linear polarization. The differences that are observed manifest themselves in significantly reduced total ion yields in the latter case, along with enhancement of lower-energy components in the kinetic-energy distribution functions measured for products of MEDI. In our experiments, multiple ionization occurs in the tunneling regime (Keldysh parameter, $\gamma \sim 0.14$).

The femtosecond laser used in the current experiments is a chirped pulse amplification, titanium-sapphire system comprising an oscillator, pulse-stretcher, regenerative amplifier, multipass amplifier, and a grating pulse-compressor. The peak energy output is 50–55 mJ per pulse, with a pulse duration of 100 fs at a repetition rate of 10 Hz. The resulting unfocused output power is ~0.5 TW. The laser pulses are temporally, spatially, and spectrally characterized at the output and at various intermediate stages. Because of dispersion in optical elements in the beam path, the final pulse duration in the interaction region is ~150 fs. Multiple ionization was studied using a linear, two-field, time-of-flight spectrometer in a large (85-cm-diam), stainless-steel, ultra-high-vacuum chamber capable of background pressures of 5×10^{-11} Torr. The spectrometer was designed such that only a subset of the total laser focal volume was sampled, thereby ensuring that only a limited range of laser intensities was accessed in the course of the measurement of mass spectra [8]. Ions were detected using a channel electron multiplier (CEM) operating in the particle counting mode. The CEM output was taken to a 100-MHz digital oscilloscope after amplification by a fast preamplifier and linked to a laboratory computer by a fast data bus. Operating pressures (with gas load) were maintained low enough (in the range 6×10^{-9}–6×10^{-8} Torr) to ensure that space-charge effects were negligible. The polarization state was varied by use of a half-wave (or quarter-wave) plate; on-line monitoring of the laser intensity ensured a constant value in the course of measurements with different polarizations.

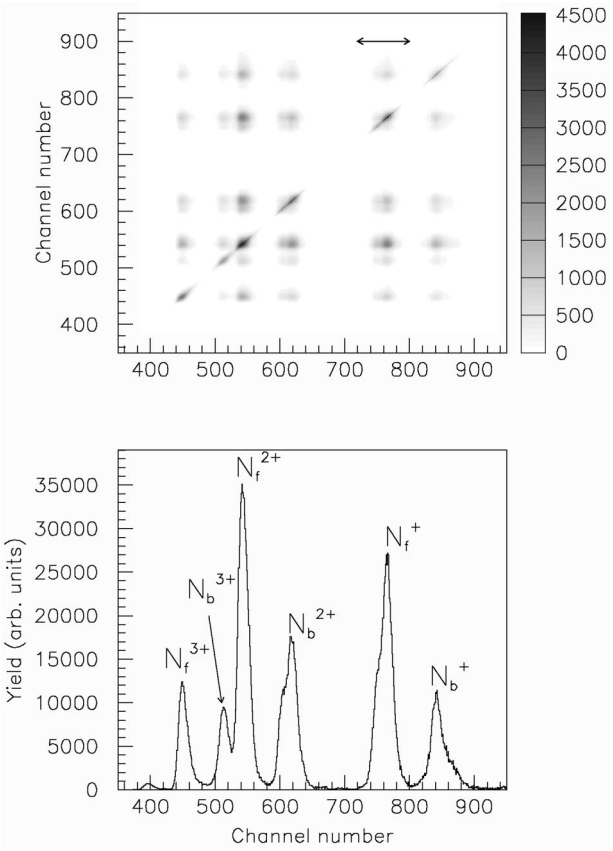

FIG. 1. MEDI of N_2 using linearly polarized light of intensity $6\times10^{15}\,\mathrm{W\,cm^{-2}}$. The top panel depicts a coincidence map; the bottom panel shows a slice of data integrated through the region indicated by the horizontal arrow. The channel numbers are proportional to ion flight time; the bottom panel indicates ions of difference *m/q* at different channel numbers. The subscripts *f* and *b* indicate forward and backward directed fragments.

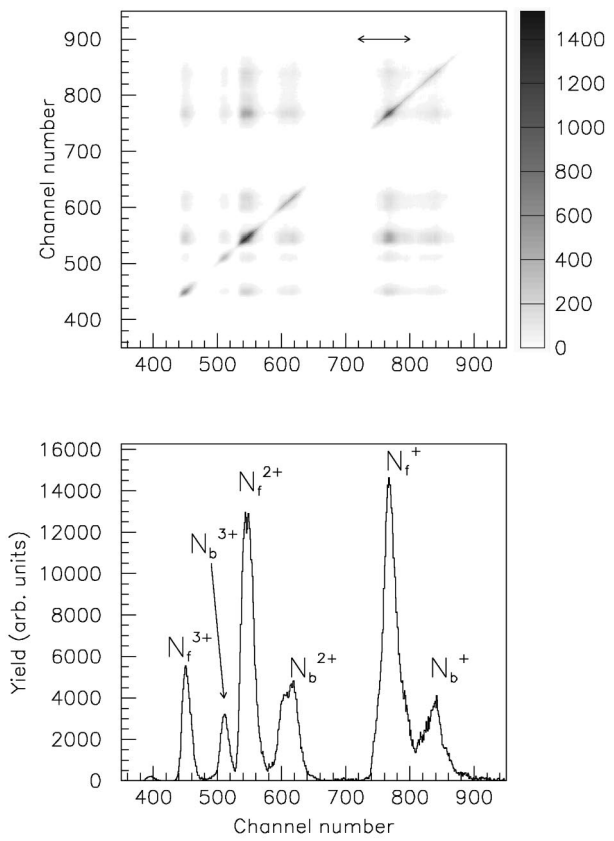

FIG. 2. MEDI of N_2 using circularly polarized light under the same conditions as in Fig. 1.

Coincidence maps obtained at a laser intensity of $2\times10^{15}\,\mathrm{W\,cm^{-2}}$ (Figs. 1 and 2) depict ion pairs that are formed upon unimolecular dissociation of N_2^{q+} ($q\geqslant2$) ions with linearly and circularly polarized light. The measurements were made using the same laser intensity in the two cases, and over a range of intensities (10^{13}–$10^{15}\,\mathrm{W\,cm^{-2}}$). Specifically, for TOF spectra measured with linearly polarized light of intensity *I*, we also made measurements at intensity 2*I* with circularly polarized light in order to establish that any differences were not simply attributable to different ionization rates in the two cases. A proper appreciation of the relative branching ratios is obtained by depicting various vertical ''slices'' through the map. By way of illustration, the lower panels of Figs. 1 and 2 show results obtained when slices are made through the forward-scattered N_b^+ channel. The N_b^+–N_b^+ coincidence channel is a reflection of the autocorrelation signal, but all other channels depict real coincidences. Note that although the morphology of the MEDI pattern remains essentially unchanged, there is a nearly threefold decrease in overall ion yield in the case of circularly polarized light. Similar decreases manifested themselves in slices through other dissociation channels (not shown). The other noteworthy difference between data obtained with linear and circular polarization lies in the energy content of the fragment ion peaks as evidenced by a preponderance of low-energy N^+ ions in the latter case. In ascribing differences in energy contents measured with linear and circular polarization, we have ensured that the acceptance angle of our TOF spectrometer is very large (~70°) for low-energy (~0.1 eV) ions under our operating conditions. In angular distribution measurements carried out in TOF instruments, the effective angular resolution of the apparatus is essentially determined by the magnitude of the ion extraction field and the kinetic-energy release (KER) associated with each fragment ion. We carried out trajectory simulations through our TOF spectrometer of ions possessing a range of KER values. Using extraction fields of $40\,\mathrm{V\,cm^{-1}}$, N^+ ions possessing high KER values (~6 eV) are detected with an acceptance angle of ~10°, whereas for N^{2+} ions with KER values as high as 20 eV, the corresponding acceptance angle is ~7°; for thermal energy ions (such as N_2^+), tests confirmed that 100% collection efficiency is obtained for all polarization states of the incident light [9].

In order to further probe the apparent enhancement of low-energy dissociation channels in measurements conducted with circular polarization, we have deduced the fragment-ion kinetic-energy distribution functions from TOF ''singles'' spectra. The kinetic-energy release (KER) distributions for $N^+ + N^+$, $N^{2+} + N^{2+}$, and $N^{3+} + N^{3+}$ forward-directed ion pairs obtained with linear and circular polarization are reflected in the slices shown in the lower panels of Figs. 1 and 2, respectively. The asymmetry that is observed in peak intensities reflects the vector addition of velocities of fragment ions that are initially directed towards and away from the TOF spectrometer [10]. The separation between the

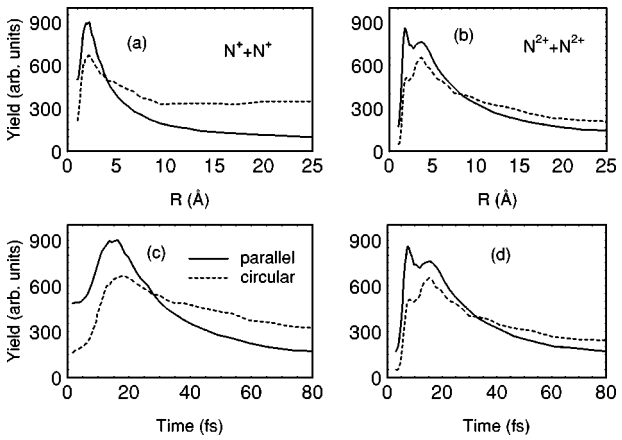

FIG. 3. Dependence of ion-pair formation on internuclear distance (a),(b) and dissociation time (c),(d) for forward-directed $N^+ + N^+$ and $N^{2+} + N^{2+}$ ion-pairs.

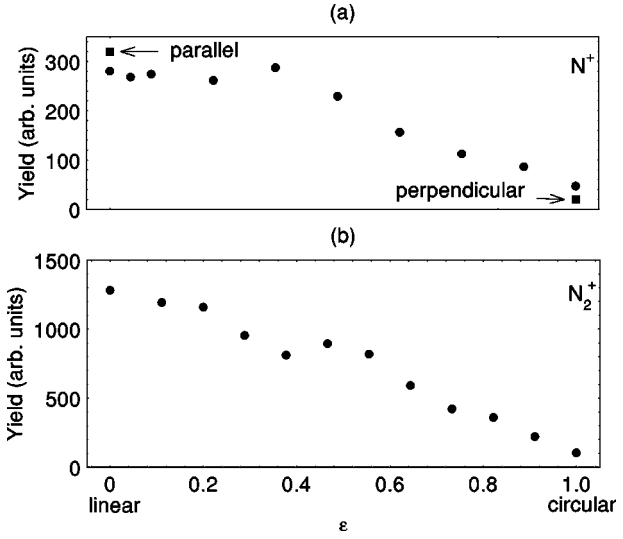

FIG. 4. Dependence of ion yield on ellipticity (ϵ): (a) N^+, (b) N_2^+.

peaks is a measure of the most probable KER upon dissociation of N_2^{2+} (for the N^+-N^+ channel) and N_2^{4+} (for the N^{2+}-N^{2+} channel). For dissociation of N_2^{2+}, these KER values were measured to be 6.7 ± 0.3 eV for linear polarization and somewhat less, 5.4 ± 0.5 eV, for circular polarization. Corresponding values obtained for N_2^{4+} in linearly and circularly polarized light were 20.0 ± 2 eV and 18 ± 3 eV, respectively. Figure 2 also provides clear evidence for formation of a larger flux of fragments with KER values that are notionally 0 eV when circularly polarized light is used. Conversely, fragment ions formed using linearly polarized light have a significantly higher propensity for larger KER values. We have considered the possibility that the lowering of KER's in the case of Coulomb explosion occurs in a plane, giving rise to significant transverse KER components for fragments. Measurements conducted at different values of ion extraction field all yielded the same apparent suppression of KER values, lending credence to our belief that the lack of unit collection efficiency for the most energetic fragments is not a major contributory factor to our results.

Values of KER reflect the internuclear separation *(r)* at which dissociation of the multiply charged molecular precursor occurs. The KER distributions can be mapped to the internuclear separation if the potential-energy function is known. In Figs. 3(a) and 3(b) we show such maps assuming Coulombic potentials [11]. The peaks in the ionization rate at ~ 2.2 Å for both linear and circular polarization are indicative of enhanced ionization at internuclear distances larger than equilibrium. Enhanced ionization (EI) of molecules in short, intense laser pulses at large critical internuclear separations R_c was initially discovered in theoretical simulations of the ionization rates of H_2^+ [6]; ionization maxima observed in the range of R_c values 2–5 Å were initially interpreted in terms of electron localization effects brought on by large charge exchange radiative resonance couplings between the highest-occupied and lowest-unoccupied molecular orbitals. Theoretical interpretations of EI in terms of extensions of the field-ionization and barrier-suppression ionization models have also been successful [12]. Experimental confirmation of EI has since been obtained in a number of studies (see, for instance, [13]), but all hitherto-reported work, both theoretical and experimental, has exclusively considered linearly polarized light. Our results indicate that EI appears to be a universal phenomenon encountered in the interaction of molecules in intense light fields, even in the circularly polarized regime. Our data also suggest that considerably larger r values are favored in MEDI with circularly polarized light.

Our observations of MEDI in N_2 obviously have no analog in atomic ionization. The molecular data enable us to readily make estimates of the time scales involved in the dissociation of multiply charged N_2^{q+} ions if we assume, in the first approximation, that the di- and tri-cation potentials are dominated by the Coulomb term [11]. Consider two atoms of reduced mass M at an initial internuclear separation of $2\beta a_0$. Following sudden ionization by a laser pulse to charge states Z_1 and Z_2, the time τ taken for the products of Coulomb explosion to develop a separation of x is [14]

$$\tau \sim \frac{\lambda_c}{2\pi c\alpha_2}\left[\frac{\beta^3 M}{2m_e Z_1 Z_2}\right]^{1/2}\left[\frac{x(1-2\beta a_0/x)^{1/2}}{2\beta a_0} + \frac{1}{2}\ln\left[\frac{1+(1-2\beta a_0/x)^{1/2}}{1-(1-2\beta a_0/x)^{1/2}}\right]\right]. \quad (1)$$

In Eq. (1), α is the fine-structure constant, m_e is the electron mass, λ_c is the Compton wavelength, while a_0 and c are the Bohr radius and speed of light, respectively. The time dependences of dissociation of N_2^{2+} and N_2^{4+} in our experiments are depicted in Figs. 3(c) and 3(d). Following Coulomb explosion, it takes 30 fs for the distance between N^+-N^+ ion pairs to become 10 Å. This time dependence is independent of the polarization state of the incident laser light. In both cases, the maximum production of N^+-N^+ ion pairs appears to occur ~ 15 fs after the initial laser pulse. It is clear from the above that enhanced ionization seems to follow the same route for linear and circular polarization. Specifically R_c is independent of the polarization state.

Figure 4 shows the variation of N^+ yield as a function of ellipticity (ϵ). These measurements were carried out using ion extraction fields ($\sim 130\ \mathrm{V\,cm^{-1}}$) that were large enough

to ensure high collection efficiency. Also shown for reference are the ion yields obtained using linearly polarized light when the polarization vector is parallel or perpendicular to the TOF axis. $\epsilon=0$ corresponds to linear polarization and the ion yield obtained is nearly the same as that with parallel polarization. As ϵ is varied the N^+ yield decreases monotonically until a minimum is obtained when $\epsilon=1.0$, which corresponds to circular polarization. At this point the ion yield is the same as that obtained when the laser polarization is perpendicular to the TOF axis. We obtained identical variations of N^{2+} and N^{3+} yields with ϵ in our experiments. These observations are consistent with recent observations of Liang *et al.* on Ar^+ yield as a function of ellipticity [3]. We have also studied the ellipticity dependence of thermal-energy N_2^+ molecular ions and the results are also shown in Fig. 4. As in the case of fragment ions, there is pronounced suppression of the parent ion. The molecular ion yield is not affected by instrumental (and KER) factors since 100% collection efficiency is ensured for thermal ions.

To summarize, our experiments on intense-field-induced multiple ionization of N_2 have revealed that the polarization state of the incident light does not affect the enhanced ionization mechanism that is established for linear polarization. The major difference we observe when using circularly polarized light is the distinct *suppression of ionization channels*. Moreover, an enhancement of lower-energy pathways to dissociation is apparent; this may reflect the importance of high-angular-momentum intermediate states that could be accessed in the case of circular polarization. Such states present ''wider'' centrifugal barriers to dissociative ionization [15]; this manifests itself in the increasing importance of longer tunneling time pathways that our data indicate. Hitherto, discussions of polarization effects in molecules have tended to focus on classical aspects of spatial alignment resulting from induced dipole moments in intense light fields. The present experiments indicate that the polarization state of light is also of fundamental importance in a quantum mechanical sense in that it affects molecular ionization yields and dissociation pathways. It is clear that such considerations need to be incorporated in the development of adequate theoretical descriptions of molecular dynamics in intense light fields.

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[1] M. Protopapas, C. H. Keitel, and P. L. Knight, Rep. Prog. Phys. **60**, 389 (1997); A. Giusti-Suzor, F. H. Mies, L. F. DiMauro, E. Charron, and B. Yang, J. Phys. B **28**, 309 (1995); E. Constant, H. Stapelfeldt, and P. B. Corkum, Phys. Rev. Lett. **76**, 4140 (1996); *Molecules in Laser Fields*, edited by A. D. Bandrauk (Marcel Dekker, New York, 1993); J. L. Krause, K. J. Schafer, and K. C. Kulander, Phys. Rev. Lett. **68**, 3535 (1992); P. B. Corkum, *ibid.* **71**, 1994 (1993); M. Yu. Kuchiev, Phys. Lett. A **212**, 77 (1996); A. Becker and F. H. M. Faisal, J. Phys. B **29**, L197 (1996), and references therein.

[2] M. Protopapas, D. G. Lappas, and P. L. Knight, Phys. Rev. Lett. **79**, 4550 (1997); A. Patel *et al.*, Phys. Rev. A **58**, R2652 (1998).

[3] K. Budil *et al.*, Phys. Rev. A **48**, R3437 (1993); P. Dietrich *et al.*, *ibid.* **50**, R3585 (1994); Y. Liang *et al.*, J. Phys. B **28**, 2757 (1995).

[4] R. A. Fox, R. M. Kogan, and E. J. Robinson, Phys. Rev. Lett. **26**, 1416 (1971).

[5] P. Lambropoulos, Phys. Rev. Lett. **28**, 585 (1972); **29**, 453 (1972); S. Klarsfeld and A. Maquet, *ibid.* **29**, 79 (1972).

[6] T. Zuo, S. Chelkowski, and A. D. Bandrauk, Phys. Rev. A **48**, 3837 (1993).

[7] The extent of elliptical polarization is defined by the ellipticity paprameter $\epsilon=E_x/E_y$. In our experiments circular polarization implies an ϵ value of 0.95–1.0.

[8] S. Banerjee, G. R. Kumar, and D. Mathur, J. Phys. B (to be published).

[9] S. Banerjee, G. R. Kumar, and D. Mathur, Pramana J. Phys. **52**, 421 (1999).

[10] G. R. Kumar, V. Krishnamurthi, and D. Mathur, Rapid Commun. Mass Spectrom. **7**, 734 (1993).

[11] For a discussion of the importance of non-Coulombic potential-energy functions, see C. P. Safvan and D. Mathur, J. Phys. B **27**, 4073 (1994).

[12] T. Seideman, M. Y. Ivanov, and P. B. Corkum, Phys. Rev. Lett. **75**, 2819 (1995).

[13] G. N. Gibson, M. Li, C. Guo, and J. Neva, Phys. Rev. Lett. **79**, 2022 (1997); J. H. Posthumus, L. Frasinski, A. J. Giles, and K. Codling, J. Phys. B **28**, L349 (1995).

[14] W. Eberhardt *et al.*, Phys. Rev. Lett. **51**, 2370 (1983); K. Boyer *et al.*, Phys. Rev. A **39**, 1186 (1989).

[15] V. Krishnamurthi, D. Mathur, and G. T. Evans, Rapid Commun. Mass Spectrom. **5**, 557 (1991).