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Femtosecond fluorescence depletion spectroscopy of NO₂ multiphoton dissociation dynamics

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Two-color femtosecond pump-probe spectroscopy has been applied to the multiphoton dissociation of NO₂ with a time resolution of ≤ 350 fs. At laser intensities in the range $\approx 3 \times 10^{12} - 2 \times 10^{13}$ W cm⁻² and a wavelength of 400 nm, NO₂ absorbs three photons before dissociation. Nascent NO $A^{2}\Sigma^{+}$ product in its n'=0 and 1 vibrational levels is probed by single-photon fluorescence depletion at 800 nm. Analyses of the ultrafast transient behavior at different intensities leads to an estimate of ≤ 600 fs for formation of NO $A^{2}\Sigma^{+}$ n'=0 and 1. © 1999 American Institute of Physics. [S0021-9606(99)03040-8]

The twin characteristics of high brightness and high temporal resolution of femtosecond laser pulses afford the capability of probing multiphoton absorption, ionization and dissociation dynamics in molecules in real time. At moderate intensities $(I \approx 10^{11} - 10^{13} \text{ W cm}^{-2})$, these processes can be understood in terms of a perturbative description of the timeevolution of wavepackets or classical trajectories over the molecular potentials accessed by the laser pulses. Pioneering work by the groups of Zewail¹ and Gerber² aimed to map out the time dependent dynamics of diatomic and triatomic molecules subsequent to multiphoton absorption. For I2 and Na₂, it was possible to pinpoint the extent of compression and extention of the interatomic distances at which resonant multiphoton absorption occurred.^{1(c),2} Similar work on K_2 has been reported by Wöste and co-workers.³ At higher intensities $(I \ge 10^{13} \text{ W cm}^{-2})$, the electric vector of the laser pulse dominates the molecular Hamiltonian such that a description of the light-matter interaction in terms of laserdressed potentials becomes more appropriate. Here a large number of studies have measured the kinetic energy partioning between dissociating fragments, and have related this information to novel phenomena such as above-threshold dissociation and ionization, bond softening and Coulomb explosions.4

This communication reports our first results on the multiphoton dissociation dynamics of NO2. This molecule has been the subject of a truly enourmous number of spectroscopic studies on account of its intense visible absorption spectrum.⁵ In the single-photon absorption regime, Wittig and co-workers⁶ have employed femtosecond pump-probe spectroscopy with a time resolution of between 0.5 and 2.1 ps to determine the energy dependence of the dissociation rate to form ground state NO $X^2 \Pi_r + O^3 P$, which proceeds via a conical intersection between the adiabatic X^2A_1 ground state and $A^{2}B_{2}$ low-lying excited state of NO₂. In the multiphoton absorption regime, a recent study of electron-ion coincidence rates by Davies et al.,7 carried out at a wavelength of 375 nm, pulse width of 100 fs and intensity of $\simeq 10^{12} \text{ W cm}^{-2}$, identified the dominant dissociative multiphoton ionization (DMI) pathway as due to three-photon excitation of NO₂ to a repulsive potential correlating with NO $C^{2}\Pi + O^{3}P$ followed by single-photon ionization of NO to form NO⁺ $X^{1}\Sigma^{+}$. In contrast, an earlier kinetic analysis by Singhal *et al.*,⁸ who employed 50 fs laser pulses at 375 nm at an intensity of 10^{12} W cm⁻², suggested that DMI occurred by single-photon absorption of the parent, dissociation via the lowest energy pathway and subsequent three-photon ionization of ground-state NO $X^{2}\Pi_{r}$. A number of other studies have addressed the mechanism of DMI as a function of wavelength and pulse width for laser intensities between 10^{13} and 2.5×10^{14} W cm⁻².⁹

In our experiments two-color femtosecond fluorescence depletion pump-probe spectroscopy has been employed to investigate multiphoton dissociation of NO2 at 400 nm. Intense femtosecond laser pulses at 800 nm were generated by a regeneratively amplified Ti:sapphire laser (Spectra-Physics Lasers). A portion of the beam was frequency doubled in a 0.5 mm BBO crystal to provide pump pulses at $\lambda_1 = 400$ nm and routed via a delay stage to generate a variable optical path length. The remainder constituted the probe pulse at $\lambda_2 = 800$ nm and was recombined with the pump by a dichroic optic so that both beams were focussed colinearly into a quartz reaction vessel. The incident pump beam intensity was varied across the range $I_1 \simeq 3 \times 10^{12} - 2 \times 10^{13} \text{ W cm}^{-2}$ by rotating a $\lambda/2$ plate before the BBO crystal, thus reducing the efficiency of second harmonic generation (SHG). The extra probe pulse energy generated at lower SHG efficiencies was compensated for by another $\lambda/2$ plate and polarizer placed in the probe beam, thereby maintaining a constant probe beam intensity of $I_2 = 10^{13} \text{ W cm}^{-2}$ in all measurements reported here. Dissociative production of NO in the n' = 0 and 1 vibrational levels of the 3sA ${}^{2}\Sigma^{+}$ Rydberg state was monitored by depleting $A^{2}\Sigma^{+}n' \rightarrow X^{2}\Pi_{r}n''\gamma$ -band fluorescence as a function of pump-probe time delay. (n')and n'' represent the upper and lower vibrational quantum numbers.) Based on Franck-Condon arguments and selection rules, we suggest that the depleting probe transition may involve $B^2\Pi \leftarrow A^2\Sigma^+$, but this band system awaits definitive spectroscopic assignment. Fluorescence was collected in a direction perpendicular to the incident laser beams, fo-

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FIG. 1. NO $A^{2}\Sigma^{+}n' \rightarrow X^{2}\Pi_{r}n''$ dispersed fluorescence spectra recorded with a spectral resolution of 1 nm: (a) n'=2 spectrum in NO resulting from two-photon absorption at $\lambda_{1}=400$ nm ($A^{2}\Sigma^{+}n'=2 \leftarrow x$ state n''=0 $+2\hbar\omega_{1}$); (b) n'=2, 1, 0 spectrum resulting from multiphoton dissociation of NO₂ at $\lambda_{1}=400$ nm. The laser intensities for both spectra are $I_{1}\approx 8\times 10^{12}$ W cm⁻² and $I_{2}=10^{13}$ W cm⁻².



FIG. 2. Femtosecond fluorescence depletion transients for multiphoton dissociation of NO₂ at different pump laser intensities at $\lambda_1 = 400$ nm: (a) for NO $A^{2}\Sigma^{+}n'=0$ formation; (b) for NO $A^{2}\Sigma^{+}n'=1$ formation. The cross correlation trace shown in (a) has a FWHM of 350 ± 30 fs. The probe pulse at $\lambda_2 = 800$ nm and $I_2 = 10^{13}$ W cm⁻² is believed to deplete NO $A^{2}\Sigma^{+}n' \rightarrow X^{2}\Pi_{r}n''$ flurorescence by single-photon excitation of the $B^{2}\Pi \leftarrow A^{2}\Sigma^{+}$ band system (see text).

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FIG. 3. Graph of the square root of the intensity of NO $A^{2}\Sigma^{+}n'=1 \rightarrow X^{2}\Pi_{r}n''=0$ fluorscence at 216 nm versus pump laser energy at $\lambda_{1}=400$ nm, demonstrating the quadratic dependence of NO $A^{2}\Sigma^{+}n'=1$ formation on pump laser intensity.

cussed onto the entrance slit of a monochromator and detected photoelectrically. In carrying out our measurements, care was taken to ensure that the detected fluorescence resulted from nascent NO $A^{2}\Sigma^{+}$ molecules produced by NO₂ dissociation: this was achieved by ensuring that the probe beam was focussed to within the volume of gas irradiated by the pump. Confirmation of the detection of nascent dissociation product was provided by comparing fluorescence spectra of NO₂ and NO in the absence of probe light (see below). Cross-correlation measurements were made by detecting sum-frequency light from an aluminum surface on which the pump and probe pulses were colinearly incident, from which the temporal resolution of the experiment was determined as no worse than 400 fs and often as short as 300 fs.

Figure 1 displays the dispersed NO $A^2\Sigma^+n'$ $\rightarrow X^2 \Pi_r n''$ fluorescence spectrum in the absence of probe laser light recorded in samples of NO and NO₂, respectively. In NO alone, two photons of the pump pulse at $\lambda_1 = 400$ nm nonresonantly excite the $A^{2}\Sigma^{+}n'=2$ level only, and Fig. 1(a) shows the spectrum of $A^{2}\Sigma^{+}n' = 2 \rightarrow X^{2}\Pi_{r}n''$ transitions, with the vibrational level assignments given in the figure. In NO₂, however, the spectrum is much more congested, showing lines arising from the n'=0 and 1 levels of the $A^{2}\Sigma^{+}$ state as well as n'=2. We attribute the appearance of emission from NO A ${}^{2}\Sigma^{+}n'=0$, 1 as due to production via multiphoton dissociation of NO₂. (NO $A^{2}\Sigma^{+}$ n' =2 is also energetically accessible at our pump wavelength and intensities, but laser intensity fluctuations have so far prevented a quantitative analysis of the NO $A^{2}\Sigma^{+}n'=2$ $\rightarrow X^2 \Pi_r n''$ spectrum in NO₂ to extract the contribution arising from dissociation.) We note that at the photon energies required to produce NO $A^{2}\Sigma^{+}$, dissociation leading to NO $X^{2}\Pi_{r}$ + O¹D products is also energetically feasible. An early photochemical study indicates that this exit channel accounts for 50% of the dissociation yield at wavelengths below 214 nm.¹⁰ It is possible to conjecture that production of NO $A^{2}\Sigma^{+}$ in the n'=0 and 1 levels may also occur either by vibrational relaxation of $n' = 2 A^2 \Sigma^+$ molecules or by nonresonant excitation of background NO. The first mechanism would result in identical forms for the transients of fluorescence depletion as a function of pump-probe time delay

which, as shown below, is not observed, whilst the second mechanism may be excluded by comparison of Figs. 1(a) and 1(b).

Figure 2 shows examples of the fluorescence from NO $A^{2}\Sigma^{+\prime}=0$, 1 at different pump-probe time delays and different pump pulse intensities. Each transient is the average of four or five individual measurements of the fluorescence depletion in real time. At large negative time delays ($\tau_D <$ -700 fs), when the probe pulse precedes the pump, the fluorescence signal is simply determined by multiphoton absorption of 400 nm NO₂ and dissociation to NO A $^{2}\Sigma^{+}$ which subsequently fluoresces over a time scale of some 100 ns. At large positive time delays ($\tau_D > 700$ fs), fluoresence from nascent NO A ${}^{2}\Sigma^{+}n' = 1$ product is depleted by the probe. In the case of NO A ${}^{2}\Sigma^{+}n' = 0$ formation, however, there is no depletion of fluorescence. We have calculated Franck-Condon (FC) factors for probe-pulse excitation of the $B^{2}\Pi \leftarrow A^{2}\Sigma^{+}$ transition with a photon energy of 1.55 eV (800 nm), assuming Morse potentials for both electronic states. For the n' = 0 vibrational level of the $A^2 \Sigma^+$ state, we find a FC factor of only 0.00721 for the $B^2 \Pi n'' = 12$ $\leftarrow A^2 \Sigma^+ n' = 0$ transition, compared to values of 0.0506 and 0.1440 for the $15 \leftarrow 1$ and $18 \leftarrow 2$ transitions, respectively. Since the transition probabilities are proportional to the square of the FC factors, the efficiency of depletion is of approximate ratio 1:49:399 for n' = 0, 1, and 2, respectively. We suggest therefore, that the different shapes of the transients for formation of NO $A^{2}\Sigma^{+}n'=0$ and 1 are simply a reflection of the different probabilities for fluorescence depletion at $\lambda_2 = 800$ nm. Since near total depletion of fluorescence can be observed, it is further suggested that excitation to the $B^2\Pi$ state facilitates probing by 1+2 REMPI.

In Fig. 2(b), the onset of fluoresence depletion at small negative values of τ_D is a result of the still high intensity of the trailing edge of the probe pulse. The decrease in fluorescence intensity at small positive τ_D values provides a measure of the time required for the dissociation of NO₂. A careful comparison of the transients in Fig. 2(b) and those obtained at other intensities with the corresponding data for depletion of NO $A^2\Sigma^+n'=2\rightarrow X^2\Pi_rn''=0$ fluorescence (not shown) enables us to set a conservative upper limit of

 $\simeq 600$ fs as the time taken for cleavage of the ON-O bond and complete separation of the incipient NO A $^{2}\Sigma^{+}$ molecule from the force field of the O ${}^{3}P$ atom. This result is in agreement with the sub-500 fs dissociation time reported by Davies *et al.* for fragmentation of NO₂ to yield NO $C^{2}\Pi$ following three-photon absorption at $\lambda_1 = 375$ nm.⁷ From this result it is possible to speculate that the fragmentation evolves via a quasibound wavepacket motion as the excited parent molecule adopts a linear Rydberg configuration prior to product separation. The enhancement in fluorescence from NO $A^{2}\Sigma^{+}n'=0$ at short positive time delays is similar to effects noted by Zewail and coworkers for multiphoton ionization of NaI^{I(a)} and HgI₂,^{1(b)} and may be attributed to a cooperative coherent effect of the temporally overlapped copolarized pump and probe pulses resulting in enhanced production of NO A ${}^{2}\Sigma^{+}$. The full-width at half maximum of the enhancement peak increases from 390 ± 30 fs to 460 ± 30 fs as the pump laser intensity is increased from $\simeq 6$ $\times 10^{12}$ W cm⁻² to $\simeq 1.2 \times 10^{13}$ W cm⁻² as shown in Fig. 2(a).

Figure 3 shows plots of the square root of the NO $A^{2}\Sigma^{+}n'=1 \rightarrow X^{2}\Pi_{F}n''=0$ fluorescence signal I_{F} as a function of the pump pulse intensity at $\lambda_{1}=400$ nm. The linear dependence of $\sqrt{I_{F}}$ on the intensity of the pump pulse is consistent with absorption of three 400 nm photons by NO₂, preparing the molecule 0.5 eV below the ionization threshold, in which absorption of the first photon to the $A^{2}B_{2}$ is resonantly saturated. Absorption of just two photons at $\lambda_{1} = 400$ nm (6.2 eV total photon energy) does not provide sufficient excitation to access the n'=0 and 1 levels of NO $A^{2}\Sigma^{+}$ through photodissociation. Keldysh parameters¹¹ of between 4.0 and 18.1 for the range of laser intensities employed here imply that any competitive ionization processes in NO₂ would be dominated by multiphoton events.

In conclusion, this communication reports results on the multiphoton absorption and dissociation dynamics of NO₂ studied by two-color femtosecond fluorescence depletion spectroscopy at $\lambda_1 = 400$ nm and $\lambda_2 = 800$ nm. An analysis of the dependence of fluorescence depletion of the product NO $A^2\Sigma^+n' \rightarrow X^2\Pi_r n''$ transition on the intensity of the pump pulse leads us to deduce that the dominant dissociation pathway at $I_1 \approx 3 \times 10^{12} - 2 \times 10^{13}$ W cm⁻² and $I_2 = 10^{13}$ W cm⁻² is initiated by absorption of three 3.1 eV (400 nm) photons. This result lends support to the mechanism pro-

posed by Davies *et al.*,⁷ who studied NO₂ multiphoton dissociation at a photon energy of 3.3 eV (375 nm) and intensity of 10^{12} W cm⁻² by femtosecond photoelectron-photoion coincidence imaging. Using sub-200 fs laser pulses, the nascent dissociation product is identified as Rydberg NO $A^{2}\Sigma^{+}$ in its n' = 0 and 1 (and probably 2) vibrational levels. From an analysis of the fluorescence depletion on the pump-probe time delay we estimate the time required for NO₂ \rightarrow NO $A^{2}\Sigma^{+}$ + O ^{3}P dissociation as no greater than 600 fs. A full quantitative understanding of the multiphoton dissociation dynamics of NO₂ requires an analysis of the time-and intensity-dependence of pump-probe photon absorption by NO₂ and NO, and this will be reported in a future publication.¹²

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