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Nonadiabatic dynamics in polyatomic systems studied by femtosecond time-resolved photoelectron spectroscopy

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We investigate the use of time-resolved photoelectron spectroscopy for studying nonadiabatic polyatomic dissociation dynamics. In particular, we emphasize the importance of the electronic structure of the ionization continuum in interpreting the results and provide an experimental example of these effects in the dissociation dynamics of the NO dimer. © *1998 American Institute of Physics.* [S0021-9606(98)03009-8]

The dissociative electronically excited states of polyatomic molecules can exhibit very complex dynamics. These cases present a challenge to high resolution spectroscopy as the spectra can often appear broad and featureless. Although the origin of such spectra is sometimes attributed to direct dissociation, broad featureless spectra can also be indicative of nonadiabatic effects. Measurements of product state distributions are likewise used to discern excited state dynamics. However, these may not be universally revealing of nonadiabatic couplings because they are sensitive to forces acting primarily in the product exit channel. Femtosecond techniques are an alternative approach to probing photodissociation and reaction dynamics in polyatomic systems.[1] In this communication, we present a femtosecond study of the photodissociation dynamics of a polyatomic molecule characterized by a diffuse absorption spectrum and a nearly statistical product state distribution, both of which conceal a more complex dynamics lying under neath. We emphasize that nonadiabatic dynamics can alter ionization cross sections, necessitating a more detailed consideration of the role of electronic symmetry in pump–probe photoionization experiments.

The nitric oxide dimer is an intriguing molecule, formed by the pairing of two $^2\Pi$ radicals. The singlet ground state is relatively strongly bound (D_0 between 600 and 800 cm^{-1}), indicating covalent character,[2] and has a *cis*-planar C_{2v} geometry[3] with an O–N–N internal bond angle of about 100°. The UV absorption spectrum is broad and featureless,[4,5] spanning the range 190–240 nm with a maximum at 205 nm. Studies of the photodissociation dynamics at 193 nm revealed that two product channels are open:[6]

$$(NO)_2^* \rightarrow NO(A\ ^2\Sigma^+ v, J) + NO(X\ ^2\Pi\ v', J') \quad (1a)$$

$$(NO)_2^* \rightarrow NO(B\ ^2\Pi v, J) + NO(X\ ^2\Pi\ v'', J''). \quad (1b)$$

At 193 nm, the energies available to channels (1a) and (1b) are 0.93 and 0.69 eV, respectively. The observed product state distributions were broad and suggested to be nearly statistical. Subsequent studies on the alignment[7,8] and vector correlations[9] of the excited state products showed weak correlations, revealing that the dissociation is not well described as occurring in the plane of the dimer. The C_{2v} excitation is

expected to be $a_1 \rightarrow b_2$ with the transition dipole moment parallel to a N–N bond. In all of these studies, the dynamics were interpreted in terms of a direct dissociation, as suggested by the diffuse nature of the absorption spectrum. In this communication, we present a study on $(NO)_2$ using both time-resolved ion and photoelectron spectroscopy to investigate the role of the electronic structure of the ionization continuum in monitoring the photodissociation process. We show that $(NO)_2$ dissociation is not direct but stepwise, due to excited state nonadiabatic couplings.

Time-resolved photoelectron spectroscopy has been suggested to be a powerful technique for the study of nonadiabatic dynamics in polyatomic systems.[10–12] The rich structure—both vibrational and electronic—of the molecular ionization continuum affords new opportunities for projecting out various aspects of wave packet evolution.[13] We note that the partial cross sections into these ionization continua depend strongly upon the electronic symmetry of the state undergoing photoionization.[14] This implies, as discussed in more detail below, that excited state nonadiabatic processes can alter the ionization cross sections into the ground versus electronically excited states of the ion.

The experimental arrangement has been previously described elsewhere.[15] Briefly, a supersonic expansion of pure NO from a pulsed nozzle produced $(NO)_2$ (ionization potential=8.74 eV) in a measured 5% concentration. This ratio was varied by changing the pulsed valve timing with respect to the lasers. Higher clusters were not observed. The skimmed beam passed through the extraction region of a photoion–photoelectron spectrometer. Both ion and photoelectron time-of-flight spectra were recorded as a function of pump–probe time delay. The femtosecond laser system used in these experiments was also described previously.[16] The pump pulse used to excite the NO dimer had a wavelength of 210 nm (260 fs, 0.25 μJ). This wavelength is nonresonant with the NO monomer. Both the dissociation product channels in Eq. (1) above are open. The probe pulse had a wavelength of 287 nm (100 fs, 1–15 μJ). The two laser beams were focused close to the molecular beam axis with a 0.8 m focal length mirror. At the interaction region, the pump intensity was around 3×10^{10} W/cm^2 whereas that of the
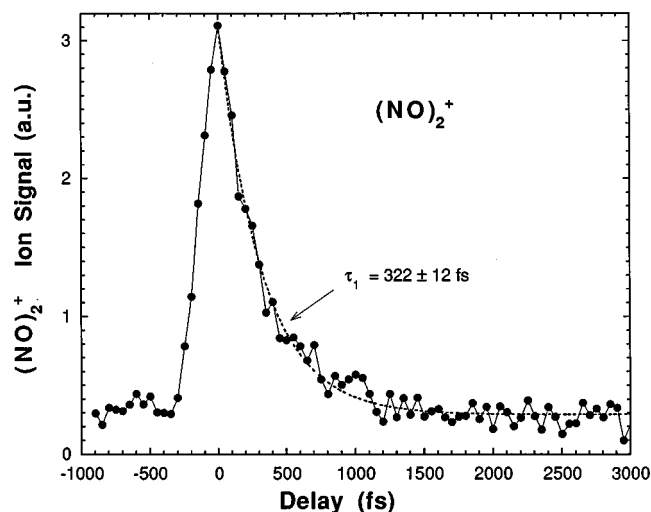
FIG. 1. The $(NO)_2^+$ parent ion signal as a function of time delay. The laser $\Delta t=0$ and cross correlation were determined via two-photon nonresonant ionization of the NO monomer. A single exponential fit (dashed line) to the data gives a time constant of 322 ± 12 fs. Upon deconvolution, the decay time is estimated to be 0.3 ps.
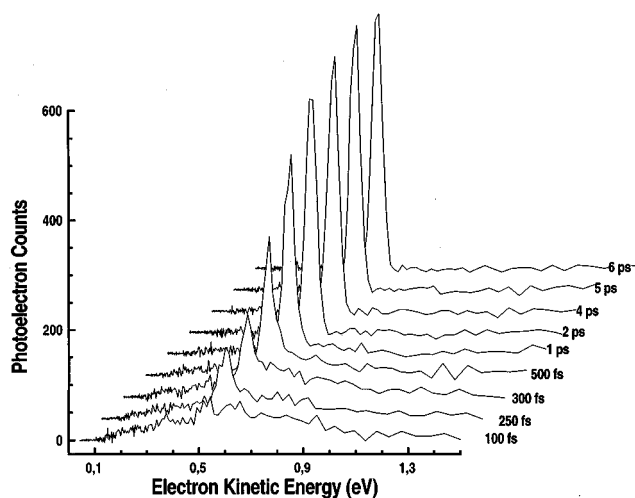

FIG. 2. Photoelectron spectra recorded as a function of time delay. The prominent peak (0.52 eV) is assigned to the $\Delta v=0$ $NO(A\ ^2\Sigma^+,v)$ $\rightarrow NO^+(X\ ^1\Sigma^+,v)$ ionizing transition. The broad background disappearing on the picosecond time scale is the photoelectron spectrum due to one-photon ionization of the $(NO)_2$ excited state.

probe was variable but not greater than 1×10^{12} W/cm^2. The latter corresponds to a ponderomotive shift of less than 8 meV, leading to a broadening of the photoelectron spectrum[17] that is less than our energy resolution (on the order of 100 meV). The 210 nm pump laser excited the $(NO)_2$, leading to dissociation. At this wavelength, the available energies are 0.42 and 0.18 eV for the $NO(A)$ and $NO(B)$ channels, respectively. The 287 nm probe laser ionized the excited $(NO)_2$ molecules, as well as the $NO(A,v,J)$ products. The absolute pump–probe $\Delta t=0$ and laser cross-correlation signal were determined by measuring the nonresonant ionization of NO monomer under molecular beam conditions in which dimers were absent. The energy calibration and resolution of the photoelectron spectrometer were determined via three-photon ionization at 287 nm of the O_2 molecule and the Xe atom, respectively. Each photoelectron spectrum was accumulated by a 200 MHz multichannel scaler over 3×10^4 laser shots.

In Fig. 1, we show a pump–probe signal of the $(NO)_2^+$ parent ion as function of time delay. A single exponential fit to the decay, shown as a dashed curve, yielded a time constant of 322 ± 12 fs. Upon deconvolution of the laser cross correlation (full width at half-maximum 280 fs), we estimate a time constant of 0.3 ps for the parent ion signal decay. This might be interpreted as the dissociation time of the excited state, being perhaps short enough to be consistent with a fairly direct dissociation, but with mixing of the out-of-plane mode (torsion) with the dissociation coordinate (N–N stretch).

In Fig. 2, we show femtosecond pump–probe photoelectron spectra for a series of time delays. These spectra have had small pump-alone and probe-alone photoelectron spectra subtracted. The prominent feature is a sharp peak at 0.52 eV which grows with time, on a broad background. The sharp peak is assigned by energy conservation to the well-known $\Delta v=0$ $NO(A\ ^2\Sigma^+,v)\rightarrow NO^+(X\ ^1\Sigma^+,v)$ ionizing

transition.[18] Neither the ground state $NO(X\ ^2\Pi)$ nor the excited state $NO(B\ ^2\Pi)$ are ionized at 287 nm: the former because of its high ionization potential, the latter, because of its unfavorable electronic configuration for one photon ionization, as well as poor Franck–Condon factors. The broad background, which also disappears on a 1 ps time scale, is the one photon photoelectron spectrum of the mixed configuration excited electronic states of $(NO)_2$. To the best of our knowledge, these $(NO)_2$ states remain uncharacterized by either experiment or theory. We expect there could be considerable state mixing: there are 16 electronic states correlating with the $NO(X)+NO(A)$ channel alone.

The appearance time of the $NO(A)$ state product, the 0.52 eV electron peak, seems considerably slower (on the order of 1 ps) than the disappearance time of the parent ion signal (on the order of 0.3 ps). In Fig. 3, we plot the integral of the $NO(A)$ photoelectron peak as a function of time delay, demonstrating the slower timescale for product appearance, suggesting a step-wise dissociation. In Fig. 3 we fit the data to a single exponential rise, yielding a time constant of 730 ±20 fs, in order to provide a single parameter to represent the average timescales involved in the product appearance. As this value is considerably longer than the decay of the initially prepared state (Fig. 1), we conclude that there are at least two steps in the dissociation. We note, however, these data cannot be fit with a simple two step rate equation model, indicating that there may be several unresolved steps in the dissociation. Pump and probe laser power studies on both the $(NO)_2^+$ parent ion signal and the 0.52 eV photoelectron signal each revealed a linear dependence and the studies at the lowest laser powers yielded the same fitted time constants as the higher powers.

We suggest that the dissociation dynamics of the NO dimer at 210 nm is not direct but stepwise via nonadiabatic interactions involving a ''dark state,'' as indicated in the proposed mechanism (2) below. The probe ionization laser
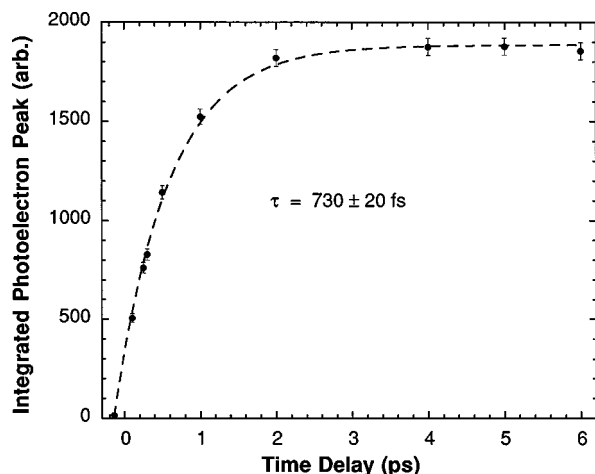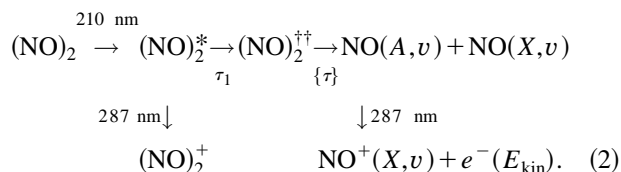
FIG. 3. The integrated 0.52 eV photoelectron peak from Fig. 2, plotted as a function of time delay. The dashed line is a best fit exponential function with a time constant of 730 ± 20 fs, yielding a single parameter representing the product appearance. This time scale is considerably slower than the decay of the initial state (0.3 ps, Fig. 1), indicating that the dissociation occurs with several steps. For a discussion, see the text.

(287 nm) creates both the $(NO)_2^+$ ion and the 0.52 eV electron signals, labeled $e^-(E_{kin})$, which are shown in Figs. 1 and 2

$$(NO)_2 \xrightarrow{210 \text{ nm}} (NO)_2^* \xrightarrow{\tau_1} (NO)_2^{\dagger\dagger} \xrightarrow{\{\tau\}} NO(A,v) + NO(X,v)$$

$$287 \text{ nm}\downarrow \qquad\qquad\qquad \downarrow 287 \text{ nm}$$

$$(NO)_2^+ \qquad\qquad NO^+(X,v) + e^-(E_{kin}). \qquad (2)$$

The initially prepared state may in fact be a superposition of several zeroth-order electronic states which exhibit ultrafast dephasing (<30 fs time scale) to the state labeled $(NO)_2^*$ in (2) above. Alternatively, there could be large amplitude motion in the initially prepared state, coupled to a nonadiabatic crossing on a slower time scale,[19] both accounting for the lack of vibrational structure in the absorption spectrum. The nonadiabatic decay of the $(NO)_2^*$ state is on a time scale of τ_1, around 0.3 ps, to a state $(NO)_2^{\dagger\dagger}$ which has relatively poor ionization cross section, presumably due to an unfavorable electronic configuration. It is this second ("dark") state which decays to the products with longer time scales $\{\tau\}$. With such a mechanism, the product state distributions would be complicated (i.e. broad) by the various curve-crossings and the alignments and vector correlations are expected to be weak, consistent with the previously reported studies.[7–9]

We believe that there is a general point to be made about the use of time-resolved ionization in studies of polyatomic dynamics. It has often been suggested as a probe technique due to its sensitivity and the universality of the photoionization process. The time-resolved parent ion signal, therefore, could arguably be used as a measure of the excited state lifetime and, hence, reaction time scale: Since photoionization is always an allowed process, as long as the molecular excited state has not dissociated to products, it may ionize (according to Franck–Condon factors) in order to produce the parent ion. This picture, however, neglects the role of the

ionization dynamics itself. Although there are no forbidden transitions in photoionization, there are propensity rules which can strongly modify integral and differential ionization cross sections. For example, if a given excited state correlates electronically with the ground state of the ion, the photoionization cross section is much larger than if it does not. The latter case would involve a two-electron process, as another electron must simultaneously rearrange in order to achieve the ground ionic state electronic configuration. Although not forbidden, this is a much lower probability event.[20] Such a state will preferentially ionize into an *electronically* excited state of the ion which has the correct core electronic symmetry. Excited state nonadiabatic effects should therefore have strong effects on ionization cross sections, the role of these processes being revealed by photoelectron spectroscopy. Since in excited polyatomic systems nonadiabatic dynamics are the rule rather than the exception, we expect that the total parent ion yield may not fully represent the chemical dynamics (i.e., dissociation time scales) of such processes. We note that other differential techniques such as time-resolved ion kinetic energy spectroscopy[1] may also be revealing of step-wise or competing dissociation processes. We believe that time-resolved photoelectron spectra from ionization into both ground and electronically excited states of the ion will yield new details about electronic population dynamics in polyatomic nonadiabatic processes.

In conclusion, we have investigated the role of the electronic structure of the ionization continuum in femtosecond photoionization studies of polyatomic systems. As an illustration of this, the dissociation dynamics of the NO dimer at 210 nm was shown to involve at least two steps and a nonadiabatic decay mechanism was inferred by comparing the time-resolved parent ion signal with the time-resolved photoelectron spectrum. These results also show how the time-resolved parent ion signal alone can be misleading in polyatomic systems. We have recently extended femtosecond time-resolved photoelectron spectroscopy further into the ionization continuum so as to include photoionization into both ground and electronically excited states of the ion.[21] This allows for a direct monitoring of electronic population dynamics, as separated from vibrational effects. We believe that studies in time-resolved photoelectron spectroscopy should reveal new details about dynamics in larger polyatomic molecules.

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