Experimental probes of dissociative states: Fano profiles in the state-specific photodissociation of FNO

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We have observed strongly asymmetric features in the $S_1 \leftarrow S_0$ state-specific photofragment yield spectrum of jet-cooled FNO. We interpret these as Fano profiles, arising from interference between direct and indirect dissociation following excitation to a region near the top of a barrier on the S_1 potential energy surface.

A major goal of photodissociation dynamics is to unravel the relationship between the electronic structure in the excited state and the subsequent nuclear dynamics.[1] The excited state potential energy surface (PES) is the main theoretical construct that reveals the intimate details of the dynamics, but it is only recently that highly accurate *ab initio* surfaces have become available.[1] Experiments on triatomic molecules are benchmarks in molecular dynamics because the small number of particles involved makes feasible both precise *ab initio* calculations and complete state specification of reactants and products. In this Communication we show that asymmetric line shapes, commonly known as Fano profiles, are useful probes of the dynamics. In particular, the partial absorption cross sections into specific product states can reveal detailed information on the shape of the PES near the Franck–Condon region and the early-time dynamics.

The $S_1 \leftarrow S_0$ absorption spectrum of FNO shows diffuse structures which can be assigned to NO-stretch and bending progressions, and calculations indicate that the quasibound resonances are superimposed on a continuum.[2,3] The *ab initio* S_1 PES has a shallow well (~ 400 cm^{-1}) and a barrier near the Franck–Condon region on an otherwise repulsive surface. The 300 K absorption spectrum shows a background contribution, but it has not been clear whether its origin is spectral congestion due to parent rotational excitation, spectral overlap due to the decay widths, or direct excitation to the continuum. In our studies, we cooled FNO in a molecular beam and measured the state-specific photofragment yield (PHOFRY) spectra by monitoring selected NO(v,J) states as a function of photolysis energy. These partial dissociation cross sections do not show a significant background contribution. However, the continuum contribution is revealed in the very asymmetric absorption line shapes, which we interpret as arising from interferences between dissociative paths that sample the well on the S_1 PES, and those that dissociate directly (Fano profiles).[4-6] Thus, our results provide experimental verification that photoexcitation indeed accesses the region near the top of the barrier. We also obtained the resonance widths (which are related to the temporal behavior) as a function of the final NO state. The dependence of the widths of these resonances on the monitored rotational state of NO gives information about the angular dependence of the PES which can be compared with recent calculations.[2] Finally, the state-specific PHOFRY spectra reveal longer bending progressions that can be seen in the 300 K total absorption spectrum.

The experimental arrangement and FNO synthesis are similar to previous work,[2] and only details specific to the present experiment are described. Premixed FNO samples (FNO:He = 50:1000 Torr) were expanded in a Ni pulsed valve driven by a piezoelectric crystal (0.5 mm diam orifice, 200 μm pulse duration) into a vacuum chamber, where the FNO was dissociated 15 mm downstream from the nozzle. A Nd:YAG laser-pumped dye laser system was frequency-doubled to generate tunable radiation between 300 and 328 nm for photolysis. The photolysis beam was collimated with a 100 cm lens located about 50 cm from the crossing with the molecular beam, producing a spot of ~ 3 mm diam at the interaction region. NO fragments were detected by laser-induced fluorescence (LIF) in the $\gamma(1,1)$ and $\gamma(2,2)$ bands.[2] Probe radiation around 226 nm was obtained from an excimer laser-pumped dye laser system with a BBO crystal. The two laser beams were counter propagating, and perpendicular both to the photomultiplier tube (PMT) and to the pulsed valve. The delay between the pump and the probe lasers was 80 ns. The bandwidth of each laser was ≤ 0.5 cm^{-1}, and each was polarized parallel to the PMT. The wavelength of the probe laser was fixed to monitor a specific NO(v,J) state, while the photolysis laser was scanned over the spectral region of interest. The observed LIF signals were normalized to both laser pulse energies, and the signals from ten laser shots were averaged for each data point.

Figure 1 shows a state-specific PHOFRY spectrum obtained while monitoring the NO($X\,^2\Pi$, $v=1$, $J=41.5$) level via the $Q_{22}(41.5)$ transition of the $\gamma(1,1)$ band. The most important features in this spectrum are the pronounced bending progression ($10v_3$) which was not fully resolved in the 300 K absorption spectrum,[7] and the marked asymmetry of several of the observed features. The solid line is a simulated spectrum consisting of five superimposed features, each fit separately to the Fano profile function,[4-6]

$$\sigma(\tilde{v}) = \sigma_0(q+\epsilon)^2/(1+\epsilon^2) + \sigma', \tag{1}$$

where

$$\epsilon = (\tilde{v} - \tilde{v}_0)/(\Gamma/2).$$

FNO Photofragment Yield Spectrum

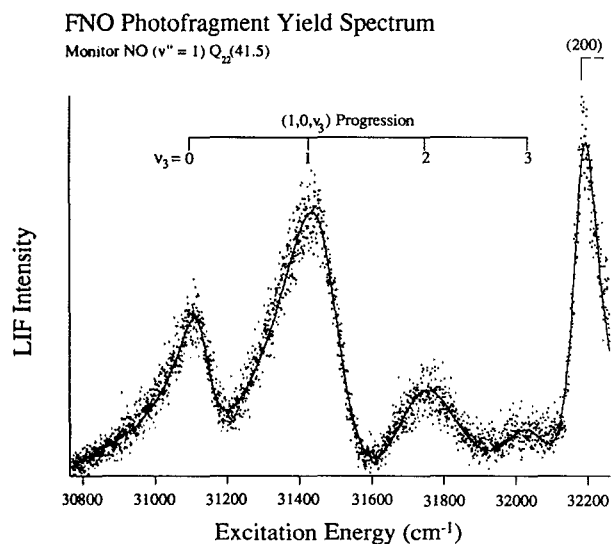Monitor NO (v'' = 1) Q_{22}(41.5)

FIG. 1. Photofragment yield (PHOFRY) spectrum of jet-cooled FNO in the region of the $S_1(10v_3) \leftarrow S_0(000)$ transition. The dots were obtained by monitoring the $Q_{22}(41.5)$ line while scanning the photolysis laser. The solid line is the sum of individual fits of each feature to a Fano profile using Eq. (1). (See the text.)

TABLE I. Fit parameters for the FNO photofragment yield spectra.[a]

Monitored NO (v, J) level	Vibrational assignment (v_1, v_2, v_3)	q	$\tilde{v}_0$ (cm^{-1})	Γ (cm^{-1})
(1,41.5)	(100)	−2.5	31 127	117
	(101)	−3.3	31 458	215
	(102)	200	31 751	278
	(103)	200	32 023	249
	(200)	4.8	32 184	89
(1,35.5)	(100)	−2.8	31 127	138
	(101)	−3.3	31 457	228
	(200)	200[b]	32 172	40
(1,33.5)	(100)	−2.1	31 141	142
	(101)	−3.2	31 451	273
	(200)	7.1	32 165	59
(1,29.5)	(100)	−2.1	31 141	157
	(101)	−5.0	31 441	363
	(200)	4.9	32 172	70
(2,29.5)	(200)	−3.5	32 173	65
	(201)	−2.1	32 528	238
	(300)	3.8	33 179	64

[a]The fits are obtained by an optimized superposition of individual fits to isolated features. As such, the fit parameters may not be unique; however, neither the signs nor the relative magnitudes are sensitive to the fit.
[b]The height of this peak is so low that a good fit is difficult to obtain.

Here $\sigma(\tilde{v})$ is the total absorption cross section, σ_0 is the background spectral absorption cross section, σ' is the cross section for absorption into a noninteracting continuum, q is the asymmetry parameter, $\tilde{v}_0$ is the center of the resonance, and Γ is the width of the resonance. A feature appears asymmetric when q is near, but not equal to, zero; when q is large ($\gtrsim 10$), the feature looks like a Lorentzian.[5,6] Notice that $\sigma(\tilde{v}) = \sigma'$ when $\epsilon = -q$. The sign of q determines the apparent shading of the spectral feature to the blue or to the red. A summary of the fit parameters used for this and other spectra is shown in Table I. The trends observed from an inspection of these parameters are that: (1) some of the peaks, especially $(v_1 00)$ and $(v_1 01)$, are strongly asymmetric; (2) there is a marked increase in q with increasing bending excitation, such that the $v_3 = 2$ and $v_3 = 3$ features appear Lorentzian; and (3) there is a general increase in Γ with increasing number of bending quanta. Thus, the state-specific PHOFRY spectra provide three parameters, q, $\tilde{v}_0$, and Γ, which are related to the topology of the excited state PES.

Figure 2 shows the two state-specific PHOFRY spectra obtained by monitoring the $Q_{22}(33.5)$ and $Q_{22}(35.5)$ transitions of the NO $\gamma(1,1)$ band following excitation in the $(10v_3)$ bands of FNO. The ratios of intensities in the two spectra reflect the partial cross sections for dissociation into the monitored NO rovibrational level, in accord with the measured NO rotational state distributions.[2] Note the change in linewidth with monitored rotational state, which is particularly large for the (102) band (e.g., compare Figs. 1 and 2).

Figure 3 displays the PHOFRY spectra obtained by monitoring the $Q_{22}(29.5)$ transition of the $\gamma(1,1)$ and $\gamma(2,2)$ bands. The upper and lower panels show excitations in the $(10v_3)$ and $(20v_3)$ bands, respectively. These two spectra have quite similar relative intensities and asymmetries of the progression members, a result of the weak coupling of the mixed bending and F–NO stretching motions to the N–O stretching motion. However, note the reduced linewidth for every line in the NO($v=2$) PHOFRY spectrum as compared with the corresponding NO($v=1$) spectrum. This is related to the dependence of the vibrationally adiabatic PES on v_1, the NO stretch.[3]

The most striking features of the spectra displayed in Figs. 1–3 are the asymmetric line shapes of many of the bands. Asymmetric line shapes from interferences between the continuum and resonant parts of wave functions are well documented in autoionization spectroscopy,[4,5] electron scattering,[6] and compound nuclear reactions.[8] They are much less common in absorption spectra of photodissociating molecules, and although several observations of Fano profiles have been reported,[5,9] we believe that this is the first example of strongly asymmetric line shapes in a dissociating polyatomic molecule that can be directly compared with theory. The strong asymmetry observed here merits a discussion of the physical origin of Fano profiles in photodissociation.

The usual interpretation of Fano profiles is based on a description of the system in terms of two weakly interacting states, one an unbound state, the other a bound discrete state, the energy of which lies within the continuum.[4] Excitation of the unbound state alone produces σ_0. The line shapes described by Eq. (1) result from interferences between these two states when they are excited simultaneously. The asymmetry parameter q is proportional to the ratio of the electronic transition moments to the discrete
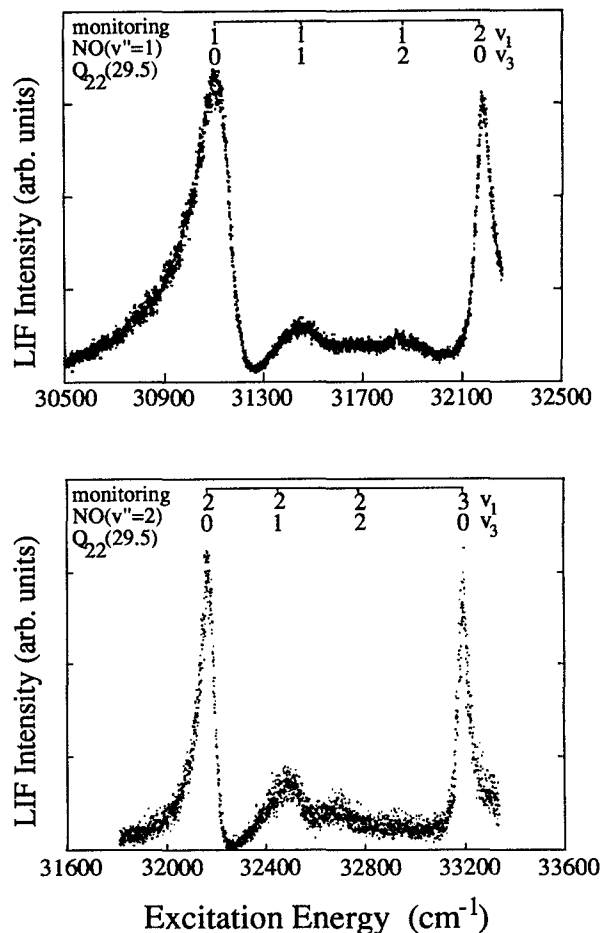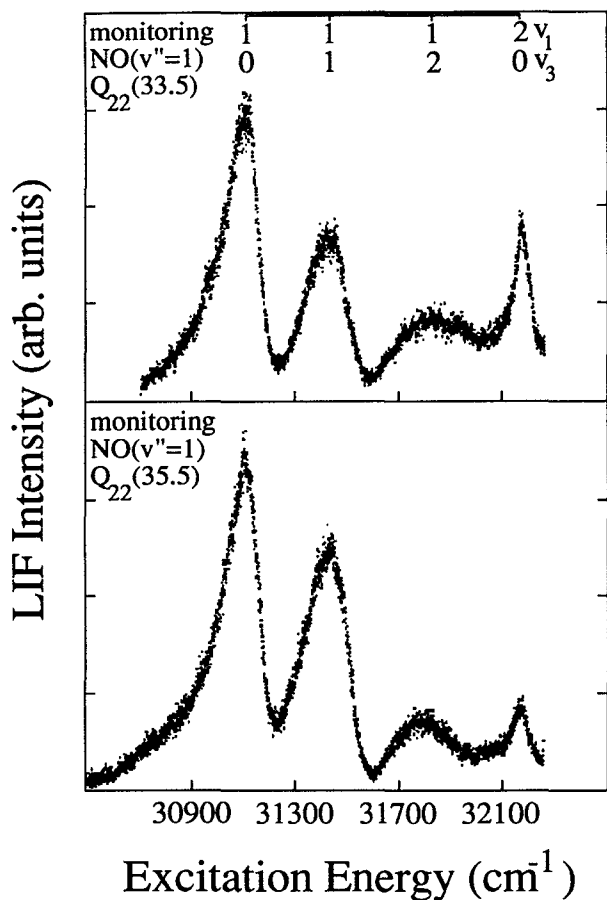
FIG. 2. Top panel: PHOFRY spectrum monitoring NO($v=1$, $J=33.5$). Bottom panel: PHOFRY spectrum monitoring NO($v=1$, $J=35.5$). The width of the (102) line, in particular, is sensitive to the monitored rotational level.

FIG. 3. Top panel: PHOFRY spectrum monitoring NO($v=1$, $J=29.5$) in the region of the $S_1(10v_3) \leftarrow S_0(000)$ transition. Bottom panel: PHOFRY spectrum monitoring NO($v=2$, $J=29.5$) in the region of the $S_1(20v_3) \leftarrow S_0(000)$ transition. Notice that these two spectra are remarkably similar, but the features of the NO($v=2$) spectrum are narrower.

and continuum states from the initial state, divided by the coupling matrix element between the discrete and continuum states. The width Γ is proportional to the square of this coupling matrix element.

Several factors can complicate this interpretation. First, when the coupling is strong, the resulting adiabatic PES has a shallow well with a low barrier to dissociation. It has been shown that Eq. (1) is accurate irrespective of coupling strength.[6] However, in this case, the evaluation of the electronic transition moments and coupling matrix elements used in the usual interpretation is not straightforward. Second, if several overlapping resonances interact with the same continuum, the observed peaks' locations and widths cannot be obtained from Eq. (1), but rather show a complicated behavior depending on their overlap.[10] Only when each overlapping resonance interacts with a different continuum and the continua do not interact with each other, is the spectrum composed of a simple superposition of the individual Fano line profiles.[10] Third, both q and Γ can vary across a single band due to the wavelength dependence of the matrix element, as mentioned by Fano.[4] Our fit assumes that q and Γ are constant within a vibronic band, but further theoretical work is needed to confirm this point. Since we were able to fit each band with a single

value of each parameter, q and Γ can be viewed as average values.

We have measured NO rotational distributions obtained in the region between the (100) and (101) resonances (e.g., at 31 200 cm^{-1}) and found that they are identical to those obtained at other excitation energies within the (101) band, but are very different from those obtained in the (100) band.[2] These results are in good agreement with dynamical calculations,[2] and suggest that the resonances interact only weakly. Therefore, a simple superposition of Fano profiles (as done in Fig. 1) may be justified, at least for the ($v_1$00) and ($v_1$01) resonances. Also, calculations predict that increasing the number of v_1 quanta slows down the dissociation, in agreement with a trend in the Γ parameters obtained from the fits. On the other hand, the small size of the off-resonance absorption suggests that there is only one continuum. The situation regarding the ($v_1$02) and ($v_1$03) resonances is less clear since these bands are broader, weaker and overlap strongly, and theoretical calculations are needed in order to fully interpret them.

With these caveats, we interpret the data in the follow-

ing manner. Time-dependent calculations on the two-dimensional $FNO(S_1)$PES (with the bending angle frozen) show that optical excitation accesses the region just above the barrier. Following excitation, the initial wave packet splits into a part that is temporarily trapped in the well, executing motions along the NO stretch and FNO bend, while another part exits directly on the repulsive side of the barrier.[3] We believe that interference between these two paths is the origin of the observed asymmetric line shapes.

When the absorption line shapes are not simple Lorentzians, the extraction of time behavior from observed linewidths is not simple. Only when the line is a Lorentzian is the time behavior a single exponential with a decay constant proportional to the observed linewidth. When the lines are asymmetric, the decay is not a simple exponential, and the full time behavior of the system can be obtained only by Fourier transformation of the entire spectrum.[1] Nevertheless, changes in the widths of observed features still indicate *relative* changes in the average decay rates of the resonances. We can contrast the behavior of FNO with the isoelectronic molecule HONO. In HONO, only the shallow well in the S_1 PES is located in the Franck–Condon region, so the wave packet is confined initially to the well and interference with the continuum is not important.[11] Indeed, the observed absorption peaks appear symmetric.[12]

The dependence of the linewidth on the monitored NO rotational level is intriguing. We find that low J levels are associated with broader bands than are high J levels (e.g., compare Figs. 1 and 3). Calculations on a two-dimensional PES (keeping the NO distance fixed) suggest that it is possible to associate each NO rotational level with a specific $FNO(S_1)$ bending angle.[2] Small and large bending angles correspond to low and high NO rotational levels, respectively. Cuts in the three-dimensional PES at different bending angles show that the PES is more repulsive when the bending angle is small (corresponding to low J's), particularly for bending levels $v_3 = 2$ and 3,[2] in agreement with our linewidth observations. Thus, the observed dependence of the linewidths on the rotational level of NO reflects changes in the PES as a function of bending angle. In contrast, increasing v_1 causes a decrease in the observed linewidth (Fig. 3 and Table I), again in agreement with the calculations.[3]

In conclusion, we have provided experimental evidence for quantum interference in the dissociation of $FNO(S_1)$; asymmetric absorption profiles arise from the simultaneous excitation of direct and indirect dissociative paths. Changes in the state-specific linewidths with the excited $FNO(S_1)$ bending level and the monitored $NO(v,J)$ level are directly related to subtle changes in the excited state PES. We emphasize that a unique interpretation of the origin of the asymmetry is made possible only by the availability of the S_1 PES. Further work is needed to directly relate features of the PES with the experimental quantities derived from the state-specific absorption profiles.

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