

LETTERS TO THE EDITOR

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COMMUNICATIONS

Fluctuations in state-selected unimolecular decomposition: Double-resonance infrared visible photofragment yield spectroscopy of NO₂

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Fluctuations in the NO(²Π) state distributions from the state-selected simple bond fission unimolecular reaction of NO₂ are probed using double-resonance photofragment yield (PHOFRY) spectroscopy. These spectra are sensitive probes of the correlation of selected NO rovibronic levels with specific resonances in the excited molecule.

In unimolecular reactions the evolution of excited resonances towards a statistical distribution of product final states is a topic of fundamental importance. Usually, in simple bond fission reactions proceeding without a barrier, the confluence of intramolecular vibrational redistribution (IVR) in the excited molecule, high density of parent states, and large number of final product states leads to a statistical outcome of energy disposal, where phase space is sampled as per the degeneracies of final states with no dynamical biases. This outcome is a manifestation of the well-known statistical assumption,¹ which states that in a microcanonical ensemble energy disposal is not dependent on the way the system arrives at the transition state (i.e., on the parent excited resonance), but only on energy, angular momentum, and parity. Statistical theories have proven quite accurate in describing both decomposition rates and product state distributions even for small molecules and with expansion-cooled samples.²

It has been recently shown that the unimolecular decomposition of NO₂ stands at the crossroads between dynamics and statistics.³ On the one hand, vibronic chaos is implicated at energies > 16 000 cm⁻¹ and is attributed to a strong nonadiabatic interaction via the asymmetric stretching mode, which results in a conical intersection of the optically active ²B₂ and the ground ²A₁ surfaces.^{4,5} Eigenstates in the vicinity of dissociation threshold ($D_0 = 25\,130 \pm 2\text{ cm}^{-1}$)^{6,7} can best be described as strongly mixed rovibronic states of predominantly ²B₂/²A₁ character.^{4,5,8} From the perspective of IVR, the application of statistical theories to describe the decomposition of NO₂ is reasonable. On the other hand, the density of states near D_0 is low and the number of final states is small and, consequently, the observation of nonstatistical features should not be surprising. Even above D_0 the spectrum is highly structured,^{3,7,9} but a progression is made from a spectral regime of mildly overlapping resonances near D_0 (i.e., $\langle \Gamma \rangle \sim 1/\langle \rho \rangle$) to severely overlapping resonances at larger excess energies, E^\dagger (i.e., $\langle \Gamma \rangle \gg 1/\langle \rho \rangle$). Thus, NO₂ provides a unique opportunity to study the transition from isolated to strongly overlapped molecular resonances above D_0 as well as correlations of the initially excited resonances with dif-

ferent product states, thereby examining the underlying causes of statistical behavior.

In previous work we have shown that the unimolecular reaction of NO₂ at $E^\dagger = 0\text{--}3000\text{ cm}^{-1}$ can be described *on average* by statistical theories, but deviations in the form of product state fluctuations around the statistical expectation exist.³ These fluctuations are observed under jet-cooled conditions at all values of E^\dagger examined, but disappear when 300 K samples are employed.^{10,11} In contrast, fluctuations in the measured decomposition *rates* of jet-cooled NO₂ samples are not observed and near D_0 the rates agree fairly well with Rice-Ramsperger-Kassel-Marcus (RRKM) theory.^{12,13} In this work we combine state-selected two-photon excitation of ²B₂/²A₁ resonances with photofragment yield (PHOFRY) spectroscopy and examine partial cross sections to specific final states. Our preliminary results show that PHOFRY spectra are remarkably sensitive probes of the evolution of resonances into specific final states, and, in particular, that state-specific effects are observed. Our data yield information on fluctuations, thermal averaging effects, inhomogeneous broadening, and the role of symmetry in the optical preparation of resonances.

The experimental apparatus and methodology have been described in detail previously.¹⁴ A pulsed molecular beam of NO₂ seeded in He was intersected by three laser beams spatially overlapped and temporally delayed. First, an infrared pulse from a tunable LiNbO₃ optical parametric oscillator (OPO, 4 mJ/pulse at $\lambda = 3.44\ \mu\text{m}$, $\sim 1\text{ cm}^{-1}$ bandwidth) tuned to the $R(2)$ line of the NO₂(101) band at 2908.5 cm⁻¹¹⁵ prepares an ensemble of vibrationally excited molecules. The OPO beam (the "idler"), which is oval in shape, is not focused and of dimension $\sim 2 \times 3\text{ mm}$ at the interaction region. The vibrationally excited molecules are dissociated after a delay of 200–300 ns by radiation from a tunable excimer pumped dye laser system. To eliminate two-photon *1-color* dissociation,¹⁶ photolysis pulse energies were 1–4 mJ in a $\sim 5\text{ mm}$ diam beam. Nascent NO(²Π) fragments were detected by laser induced fluorescence (LIF) on the $\Delta v = 0$ sequence of the γ system, using the frequency doubled output of a second excimer

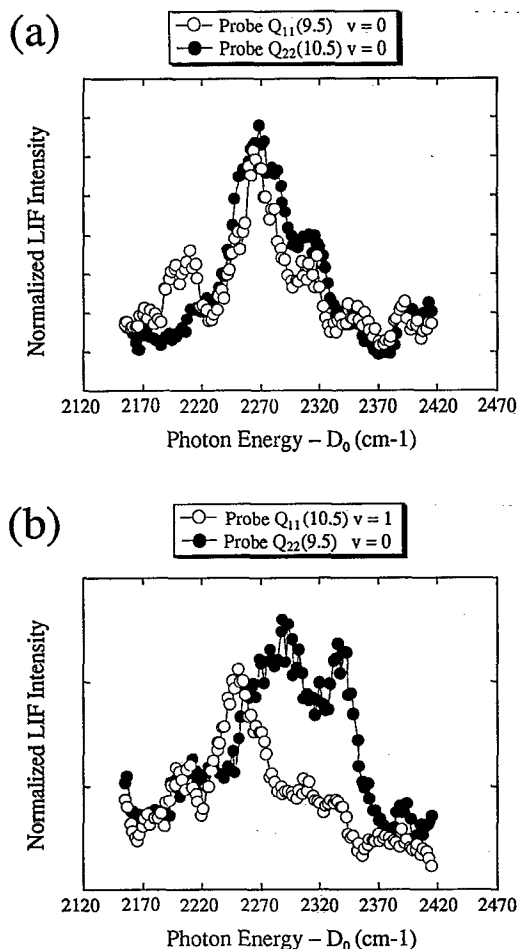


FIG. 1. Single-photon PHOFRY spectra of NO_2 at $E^\dagger=2150\text{--}2450\text{ cm}^{-1}$ obtained by monitoring: (a) the $Q_{11}(9.5)$ vs $Q_{22}(10.5)$ transitions of the (0,0) band of the NO γ system and (b) the $Q_{11}(11.5)$ vs $Q_{22}(10.5)$ transitions of the (0,0) and (1,1) bands of the NO γ system, respectively.

pumped dye laser system delayed by 200 ns with respect to the photolysis laser. One- and two-photon PHOFRY spectra were obtained by fixing the probe laser frequency to a specified rovibrational transition in a selected band of the NO γ system and scanning the photolysis laser frequency to obtain a relative partial cross section for dissociation into the monitored state.

In simple bond-fission unimolecular reactions, PHOFRY spectra are usually either largely unstructured,^{2,17} or show similar structures for all monitored levels.^{2,18} In NO_2 , while similarities are observed in the PHOFRY spectra obtained by monitoring different product states, clear differences are manifest as well. This is evident even in jet-cooled spectra obtained without further parent state selection, and Fig. 1 displays several one-photon spectra in the range $E^\dagger=2150\text{--}2450\text{ cm}^{-1}$. The spectra in Fig. 1(a) were obtained by monitoring adjacent rotational levels in NO ($v=0$), while those of Fig. 1(b)—by monitoring similar rotational levels in $v=0$ vs $v=1$. In each spectrum a prominent structure is observed of width $> 50\text{ cm}^{-1}$ full width at half-maximum (FWHM), much broader than expected solely from lifetime broadening.^{12,13} The spectra shown in Fig. 1(a) exhibit a clear correlation in the posi-

tions and intensities of the structures within the clump, while those shown in Fig. 1(b) exhibit a much poorer correlation. These results, repeated with other levels as well,¹⁹ show that adjacent rotational states within the same vibrational manifold originate from similar resonance structures but the separate vibrational manifolds correlate with different resonances, reflecting differences in the projections onto the transition state. This result is also shown in spectra which compare $v=0$ vs $v=1$ rotational levels at the same total NO rovibrational energy.¹⁹

To gain more detailed insight regarding correlations, we obtained double-resonance IR/visible PHOFRY spectra. Note that, at rotational temperatures of 3–5 K, the primary levels populated in the NO_2 parent are $N=0$ ($\sim 20\%\text{--}45\%$), $N=2$ ($\sim 50\%\text{--}55\%$), and $N=4$ ($\sim 5\%\text{--}20\%$) of the $K=0$ stack, which are of (+) total parity and A_1 spin-rovibronic symmetry. Single photon excitation accesses levels of (–) total parity, A_2 symmetry, and total angular momentum $J=1/2\text{--}11/2$. However, double-resonance excitation via the $R(2)$ transition of the (101) band accesses levels of A_1 symmetry, (+) total parity, and total angular momentum $J=3/2\text{--}9/2$. A different subset of resonances is thus prepared via one- vs two-photon excitation, with the total number of allowed transitions reduced by more than a factor of 2 in the state-selected spectra.

Figure 2 displays two pairs of one- vs two-photon PHOFRY spectra obtained in the range (a) $E^\dagger=485\text{--}620\text{ cm}^{-1}$ and (b) $E^\dagger=2150\text{--}2450\text{ cm}^{-1}$ by monitoring the $Q_{11}(11.5)$ and $Q_{11}(25.5)$ transitions. In each panel, marked differences in the positions and intensities of the resonance structures are observed, which reflect both the differences in optical selection rules and the scattering matrix elements to the monitored final state. We note that the rotational state distributions of the $\text{NO}(^2\Pi)$ fragment obtained at the same E^\dagger by using one- vs two-photon excitation are both statistical on average but exhibit quite different fluctuation patterns, thereby showing that energy disposal is sensitive to the initially excited resonance.²⁰ Further inspection shows that the double-resonance spectra are not obviously more highly structured than the one-photon ones, and additionally, do not exhibit a clear loss of structure with increasing E^\dagger . In fact, some spectral features in the double resonance PHOFRY spectra obtained at $E^\dagger=2000\text{--}2500\text{ cm}^{-1}$ are much narrower than expected from the average decomposition lifetimes.²⁰ The absence of correlations between the lifetimes and linewidths reflects interferences among coherently excited overlapping resonances as discussed by Mies,²¹ which can cause the appearance of narrow structures and multiexponential decay profiles even for fast dissociations,²² and renders unjustified the extraction of lifetime information from frequency domain data.

Correlations based on total angular momentum are also evident in our spectra, as shown in Fig. 1(a) and also in Fig. 3(a), which displays IR/visible double-resonance spectra at $E^\dagger=460\text{--}635\text{ cm}^{-1}$ obtained by monitoring the $R_{11}(6.5)$ vs $Q_{11}(5.5)$ transitions. The spectra are highly structured and quite similar when the monitored levels dif-

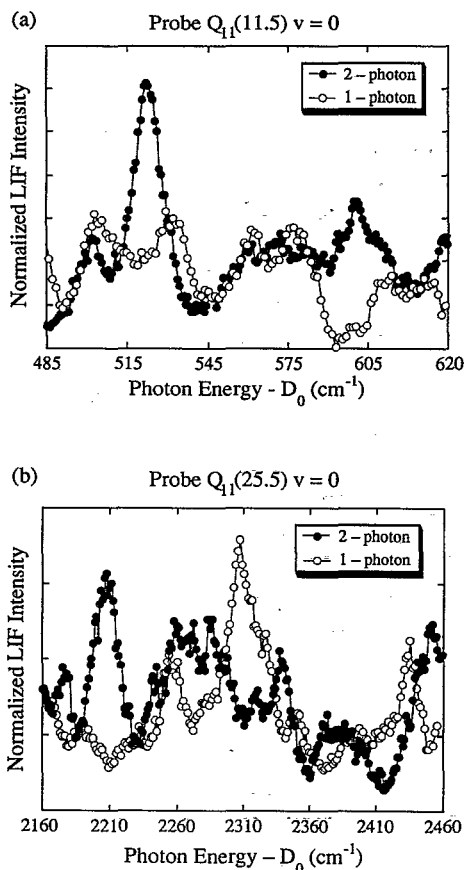


FIG. 2. Single-photon vs double-resonance IR/visible PHOFRY spectra of NO_2 obtained by monitoring; (a) the $Q_{11}(11.5)$ transition of the (0,0) band of the NO γ system at $E^\ddagger=460\text{--}635\text{ cm}^{-1}$, and (b) the $Q_{11}(25.5)$ transition of the (0,0) band of the NO γ system at $E^\ddagger=2150\text{--}2450\text{ cm}^{-1}$.

fer by $\Delta J=1$. In contrast, compare the $R_{11}(6.5)$ vs $Q_{11}(11.5)$ spectra ($\Delta J=5$) displayed in Fig. 3(b), which show more pronounced differences. This trend is reproduced at all examined E^\ddagger both in double-resonance and in one-photon PHOFRY spectra,^{19,20} supporting the view that product states of similar total angular momentum arise from the same subset of resonance states. This is also reflected in the fluctuation patterns observed in the NO rotational distributions obtained at $E^\ddagger=0\text{--}3038\text{ cm}^{-1}$, which tend to show pronounced structures with widths on the order of several J s.³ This result may reflect differences in the composition of the resonance states in terms of molecular eigenstates that project onto different fragment rotational levels via the transition state.

In summary, we have used double-resonance IR/visible PHOFRY spectra to probe the evolution of excited-state resonances to final product states in a unimolecular reaction that on average is well described by statistical theories, and have observed clear correlations between selected final states and groups of resonances. The lack of correlation between the observed linewidths and the measured decomposition lifetimes, as well as the persistence of fluctuations at high E^\ddagger suggest that a theory based on coherent excitation of overlapping resonances and their projection onto final product states via the transition state

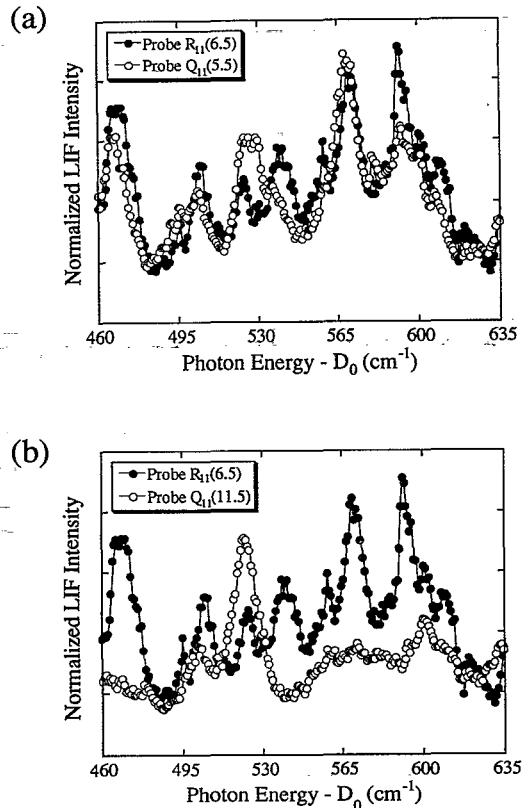


FIG. 3. Double-resonance IR/visible PHOFRY spectra of NO_2 obtained by monitoring; (a) the $R_{11}(6.5)$ and $Q_{11}(5.5)$ transitions and (b) the $R_{11}(6.5)$ and $Q_{11}(11.5)$ transitions of the (0,0) band of the NO γ system.

should be able to account for our observations.^{22,23} Further work along these lines is in progress.

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