VIBRATIONAL STATE DEPENDENCE OF THE $\tilde{A}$ STATE LIFETIME OF HONO

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Lower limits to the subpicosecond lifetimes of specific vibrational levels of the quasistable $\tilde{A}$ state of HONO are obtained through photodissociation experiments in a supersonic jet. Laser-induced fluorescence of the OH fragment ejected by the $\tilde{A}$ state of HONO is used as a probe for $\tilde{A}$–$\tilde{X}$ absorption of the parent. The excited-state lifetime, estimated through $\tilde{A}$–$\tilde{X}$ absorption widths measured by scanning the photodissociation wavelength, shows a dependence on the number of quanta of the optically accessible -N=O stretching (ν_2) vibration and is interpreted in terms of the topology of the $\tilde{A}$ state surface.

State-selected photodissociation studies of molecules with more than three atoms can, in principle, provide probes for the dynamics of energy transfer processes. For example, if an optically excited vibration in a parent is coupled to another vibration that evolves into a degree of freedom in a photofragment, the dependence of the fragment energy content with the photoselected vibration could be used as a probe for V→V type of transfer [1,2]. If the excited vibration is coupled to the fragment recoil coordinate, then the process is akin to V→T processes. This coupling is somewhat hard to probe because fragmentation of electronically excited polyatomic molecules is often very fast, so that real-time measurements are difficult. However, frequency-domain measurements can be used to monitor the recoil coordinate. For example, resonance Raman studies provide information about the "intermediate" time domain [3], and the parent's lifetime-limited absorption linewidths are sensitive to the "early" dynamics (in the Franck–Condon region).

We have been interested in the photodissociation of the quasi stable $\tilde{A}$ state of HONO and DONO because these molecules provide an opportunity to study some of the above dynamical consequences of coupling between internal coordinates [1,2]. In addition, these systems are small enough that it should be possible to generate reliable ab initio potential energy surfaces and compare trajectory calculations with experimental results. The normal vibrational modes of HONO are shown in table 1. The $\tilde{A}$–$\tilde{X}$ transition involves promotion of an electron from a nonbonding orbital centered on the terminal O atom to the lowest π^* orbital between the nitrogen and the terminal oxygen [4,5]. Excitation of the $\tilde{A}$ state therefore lengthens the N=O bond, and is accompanied by a progression in the N=O stretching vibration ν_2 [4]. Consequently, a wide range of vibrational states can be optically accessed, so that it is possible to systematically probe the dynamical consequences of coupling between ν_2 and other degrees of freedom. For example, our recent experiments [1,2] on the fragmentation of trans-DONO($\tilde{A}$) have sought to probe the consequences of coupling between the ν_2 vibration and the in-plane DON angle-bending motion ν_3. Spectroscopic work of King and Moule [4] showed that ν_3 is coupled to

Table 1
Vibrational modes of HONO

Vibration	Description
ν_1	O-H stretch
ν_2	N=O stretch
ν_3	HON bend
ν_4	O-N stretch [a]
ν_5	ONO bend
ν_6	OH torsion

[a] The recoil coordinate.

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ν_2 in DONO($\tilde{A}$) and not in HONO($\tilde{A}$). Since ν_3 is the predominant contributor to the OD (OH) fragment's in-plane angular motion, the above coupling manifests itself in the form of higher in-plane rotation and orbital alignment in OD than in OH. In addition, this effect in DONO is a function of the number of ν_2 quanta excited in the parent.

In this paper, we describe experiments aimed at probing the coupling between the ν_2 (N=O) vibration with the recoil (O–N) coordinate ν_4. The presence of this coupling is suggested by the following observations: (a) The N=O stretching frequency (1139 cm^{-1}) in HONO($\tilde{A}$) is quite different from that (1904 cm^{-1}) in the free NO(X) photofragment. (b) As mentioned previously, the HONO $\tilde{A}$–$\tilde{X}$ excitation involves an $n \rightarrow \pi^*$ excitation in the –N=O chromophore, so that the energy in excess of the dissociation threshold is initially "localized" at this site. A substantial part of this energy eventually appears along the recoil (central O–N) coordinate ν_4, as indicated by the fragment Doppler profile [6,7]. Here, we wish to probe if the motion along O–N (i.e. the *rate* of fragmentation) is influenced by the number of ν_2 quanta. One might expect to observe this experimentally, for example, in the form of ν_2 dependence of $\tilde{A}$–$\tilde{X}$ linewidths. There is a slight hint of this effect in the HONO absorption spectrum shown by King and Moule (fig. 1 of ref. [4]), but this is not conclusive because of limited experimental resolution in the reported spectrum and the usual congestion problems in room temperature experiments. Here, we describe experiments performed in a supersonic jet so that only low rotational states are populated[#1].

In the present experiments HONO, prepared through the $H_2O+NO_2+NO = 2HONO$ reaction, is mixed with argon (total pressure ≈400–500 Torr) and rotationally cooled by expanding through the 500 μm orifice of a pulsed valve into a reaction chamber. The rotational temperature as judged by measurement of the excitation spectrum of NO_2, which coexists with HONO in our sample, is ≈4–6 K. The photodissociation beam is generated by either frequency-doubling the output of a LD700/LDS698/DCM dye laser, pumped by the second harmonic of a Nd^{3+}:YAG laser, or by pumping a BBQ dye laser with the third harmonic of the pump laser. The probe is generated by exciting a rhodamine 590+610 dye laser with the second harmonic of the same pump laser, and is optically delayed by ≈20 ns with respect to the photodissociation beam. The HONO $\tilde{A}$–$\tilde{X}$ absorption is mapped by parking the probe at the strongest feature ($Q_1(1)+{}^QP_{21}(1)+R_2(3)$ lines) in the A–X (1, 0) excitation spectrum of the OH fragment and scanning the photodissociation wavelength. A portion of the "excitation spectrum" of HONO thus obtained is shown in fig. 1. We note that King and Moule's assignments [4] for cis-HONO were uncertain by one quantum of ν_2' because of spectral congestion. The congestion is reduced in the present experiments due to supersonic cooling, allowing identification of the origin (0_0^0) band of the cis isomer as a weak shoulder to the 0_0^0 transition of the trans-isomer. In the present assignments for cis-HONO, the excited-state ν_2 content is thus higher by one quantum.

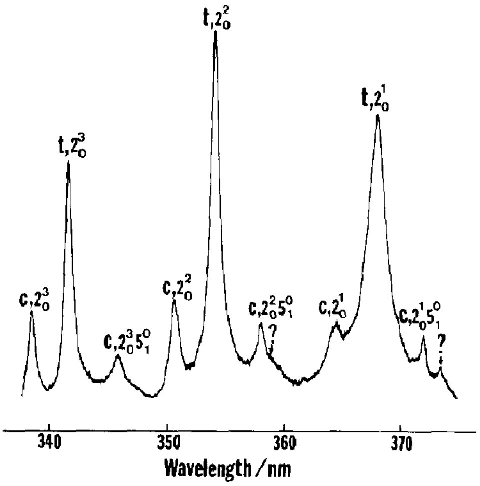

Fig. 1. Part of the "excitation spectrum" of HONO obtained by fixing the frequency of the probe laser at the strongest feature ($Q_1(1)+{}^QP_{21}(1)+R_2(3)$ lines) in the (1, 0) A–X transition of the OH fragment, and scanning the photodissociation wavelength. The absorption due to the trans and cis isomers are identified by the letters t and c, respectively, attached to each transition. The spectrum shown is a composite of regions scanned with LD700, LDS698 and DCM dyes in the photodissociation dye laser. Unassigned transitions are marked by "?".

[#1] Room temperature experiments, using the same technique as that used here with HONO at 5–6 K, show $\tilde{A}$–$\tilde{X}$ profiles that are slightly broader due to ground state rotational distribution. Lowering the rotational temperature of HONO also increases the resolution between adjacent vibronic transitions.

The photolysis bandwidth used in the present work is ≈0.9 cm^{-1}. Absence of unresolved structure underneath the absorption features recorded at this resolution is verified through measurements with a bandwidth of ≈0.12 cm^{-1}, attained by inserting an etalon in the cavity of the photolysis dye laser. The measurements, reported in table 2, are not contaminated by the ≈0.9 cm^{-1} bandwidth used because the inherent $\tilde{A}$–$\tilde{X}$ widths are much larger. We note that the subpicosecond lifetimes (table 2) deduced from the present frequency-domain measurements are consistent with previous observation of fragment Doppler profiles characterized by an asymmetry parameter β that is close to the limiting value of -1 [#2], implying lifetimes much shorter than the molecular rotational period [6,7].

The HONO $\tilde{A}$–$\tilde{X}$ absorption widths reflect recurrences in the early dynamics in the Franck–Condon (FC) region. Consequently, the dephasing lifetimes implied by the observed widths refer to the disappearance from the FC region and are therefore sensitive to the $\tilde{A}$ state topology in this region. We note that the width is the largest for the 0^0_0 transition, smaller for 2^1_0, and decreases further to the blue (table 2), implying an opposite trend for the lifetime in the FC region.

Table 2
The lifetimes (τ) of HONO($\tilde{A}$), estimated from experimental $\tilde{A}$–$\tilde{X}$ widths (fwhm)

	State	Width (cm^{-1})	τ (fs)
trans HONO	0^0	245(±30)	22
	2^1	120(±10)	44
	2^2	60(±5)	88
	2^3	55(±5)	96
	2^4	75(±15) [a]	71
cis HONO	2^2	60(±5)	88
	2^3	55(±5)	96
	2^4	60(±10)	88

[a] The error associated with the measured width for the 2^4 state is quite large and thus, within experimental error, the lifetime is the same as those for 2^2 and 2^3 states.

Qualitative features of the $\tilde{A}$ state surface that are capable of explaining the observed trends in the lifetimes of trans-HONO are shown in fig. 2 [#3]. As indicated by the $\tilde{A}$–$\tilde{X}$ widths and also by other observations described previously, the N=O coordinate is coupled to the recoil O–N axis, so that the mechanism for $\tilde{A}$ state fragmentation involves vibrational predissociation. The short duration (≈22 fs) of the 0^0 state suggests that the associated trajectory undergoes ≲1 oscillation along the N=O coordinate [#4] before leaving the FC region along the recoil coordinate. The ≈45 fs duration of the 2^1 state implies <2 oscillations along the N=O coordinate. The longer lifetime for this state compared to that for 0^0 is intriguing, and suggests that the increased kinetic energy along N=O in this case makes it somewhat more difficult for the associated trajectory to be guided from the FC region towards the "bottleneck (shown in fig. 2) by the surface slope/curvature along the O–N coordinate. This increases the number of recurrences through the FC region. Increasing the $\tilde{A}$ state ν_2 content further increases this effect. For example, the 2^2 state survives for ≈90 fs, corresponding to ≈3 N=O oscillations. It is thus clear that the lifetime variations deduced from the $\tilde{A}$–$\tilde{X}$ widths are due to differences in the number of recurrences in the early dynamics of the fragmentation process. These are sensitive to the excited state topology in the Franck–Condon region and the bottleneck along the O–N coordinate, and should thus provide tests for ab initio $\tilde{A}$ state surfaces. We note that a recent calculation [9] is somewhat deficient because it predicts a ν_2 dependence of $\tilde{A}$–$\tilde{X}$ width that is opposite of the observed trends (table 2).

In summary, the efficiency of energy transfer in HONO($\tilde{A}$) from the N=O to the recoil O–N coor-

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[#2] The asymmetry parameter $\beta = 2P_2 \cos\vartheta = -1$ when the angle ϑ between the parent transition moment and the recoil axis is 90°, as in the $\tilde{A}$–$\tilde{X}$ transition of HONO. If the excited state lifetime is long enough, it can blur the fragment Doppler profile due to parent rotation prior to fragmentation. Therefore, the experimental (effective) β can be used as a measure of the lifetime of the unstable state. See, for example, ref. [8].

[#3] That the surface is somewhat flat (with perhaps a small dimple) along O–N in the FC region is suggested by ab initio calculations [5]. It was also proposed previously by us [6] and was based on Pack's work [9] on diffuse structured spectra of polyatomic molecules. The surface shown in fig. 2 has a narrower "bottleneck" than that in ref. [10], thus providing a possible explanation (see text) for the state dependence of the $\tilde{A}$ state lifetime shown in table 2.

[#4] The N=O vibrational frequency of 1139 cm^{-1} corresponds to an oscillation period of ≈29 fs.

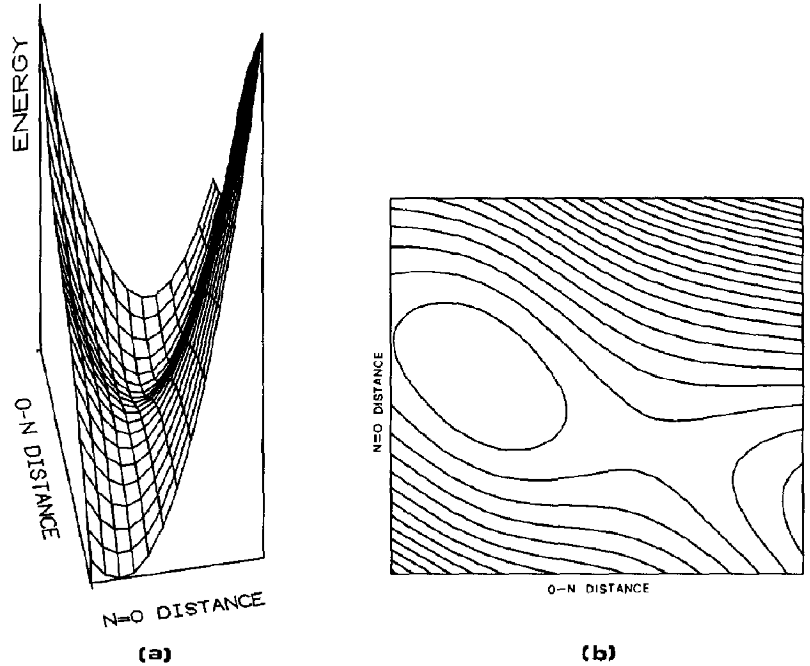

Fig. 2. (a) Qualitative features of the $\tilde{A}$ state surface consistent with the observed ν_2 dependence of the lifetime in the Franck-Condon region (see text). (b) Contour diagram of the surface. The predominant change accompanying the $\tilde{A}$–$\tilde{X}$ transition is a lengthening of the N=O bond length [4]. Franck-Condon considerations would thus suggest that trajectories on the $\tilde{A}$ state start near the inner turning point along the N=O coordinate.

dinate (V→T transfer) depends on the number of ν_2 quanta. Experiments on the isotopic cousin DONO shows a similar ν_2–ν_4 coupling. In addition, as shown recently [1,2], there is evidence for coupling of ν_2 with the in-plane DON bending motion ν_3, so that the overall energy-transfer effects in this case are akin to those in V→V+T processes. It is thus clear that these results, together with experiments on the energy distribution, rotational and orbital alignments, and translational anisotropy of the photofragments [1,2,6,7,11] provide ample tests for future ab initio calculations of the $\tilde{A}$ state surface near the Franck–Condon region and in the exit channel.

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