J. Phys. Chem. A **1998,** *102,* 2297−2301

$\tilde{B} \leftarrow \tilde{X}$ Vibronic Spectra and $\tilde{B}$-State Fluorescence Lifetimes of Methylvinoxy Isomers

Sarah Williams, Eyal Zingher,[†] and James C. Weisshaar*

Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706-1396

Received: December 8, 1997

Jet-cooled laser-induced fluorescence spectra of the $\tilde{B} \leftarrow \tilde{X}$ electronic transition of 1-methylvinoxy and of a cis/trans mixture of 2-methylvinoxy are presented. We observe some 50 vibronic bands in the spectrum of 1-methylvinoxy. The complexity is due to a change in the preferred methyl rotor orientation on electronic excitation. The $\tilde{B}$-state barrier to internal rotation is approximately 750 cm^{-1}. The $\tilde{B}$-state fluorescence lifetimes decrease from about 130 ns near the origin to 26 ns for internal energy of 2700 cm^{-1}. We observe some 22 vibronic bands in the spectrum of the cis/trans mixture of 2-methylvinoxy. The $\tilde{B}$-state fluorescence lifetimes decrease gradually from about 190 ns near the origin to 140 ns for internal energy of 1170 cm^{-1} and then very sharply at higher energy. The new spectra serve as fingerprints for identification of specific methylvinoxy isomers as products of chemical reactions of O(^{3}P) with alkenes, as recently observed by Bersohn and co-workers.

Introduction

Vinoxy radicals are important in combustion chemistry as one primary product of reactions of O(^{3}P) atoms with alkenes.[1−4] The near-UV $\tilde{B}-\tilde{X}$ electronic spectrum of jet-cooled vinoxy radical[5] provides a useful way to identify this product and potentially to monitor its subsequent chemical kinetics.[6, 7] That spectrum has been extensively studied by laser-induced fluorescence (LIF),[8−10] by hole-burning spectroscopy,[11] and most recently by two-color resonant four-wave mixing spectroscopy (TC-RFWM).[12]

In this paper, we report jet-cooled $\tilde{B}-\tilde{X}$ LIF spectra of the substituted vinoxy radicals 1-methylvinoxy and 2-methylvinoxy. These new spectra are useful in corroborating the identity of more complex reaction products. Indeed, a hotter version of our 2-methylvinoxy spectrum has recently been observed following the reaction O(^{3}P) + isobutene.[13] Similarly, a hotter version of our 1-methylvinoxy spectrum has recently been observed following the reaction F + acetone.[14]

The new methylvinoxy spectra also begin to address the unresolved issue of the barrier to internal rotation of a methyl group near a radical center. Better intuition about methyl rotor behavior is needed to build sensible statistical models of the unimolecular reactions of hot organic radicals in combustion systems.[15] The density of rotation−torsion−vibrational states that enters statistical rate theory depends sensitively on whether each methyl rotor is free or experiences a substantial hindering potential. The same types of barriers are also important in mechanistic organic chemistry. We need simple but realistic models of the electronic factors underlying these noncovalent interactions.[16]

We also report $\tilde{B}$-state fluorescence lifetimes for a variety of upper levels in both 1-methylvinoxy and 2-methylvinoxy. As in vinoxy itself,[12,17] we find that the methylvinoxy lifetimes decrease slowly just above the $\tilde{B}$-state origin and then abruptly beyond a certain excitation energy, signaling the sharp onset of a nonradiative decay process. Intriguingly, across the three molecules vinoxy, 1-methylvinoxy, and 2-methylvinoxy this onset occurs at nearly constant total excitation energy above the ground state (29 900−30 200 cm^{-1}) rather than at nearly constant vibrational energy within the $\tilde{B}$ state (E_{vib} = 1200−2700 cm^{-1}).

Experimental Section

As before,[18] we create useful number densities of internally cold radicals by excimer laser photolysis of suitable precursors upstream in a pulsed nozzle expansion of 2−3 atm of Ar behind a 1.0 mm diameter nozzle (General Valve). The target radicals are 1-methylvinoxy and 2-methylvinoxy (Figure 1); the latter can have both cis and trans isomers. In earlier work, Miller and co-workers[9] produced vinoxy itself, CH_2CHO, by 193 nm photolysis of ethyl vinyl ether, $C_2H_5OC_2H_3$. By analogy, we prepared 1-methylvinoxy by 193 nm photolysis of methyl isopropenyl ether, $CH_2{=}C(CH_3)OCH_3$, obtained commercially from Fluka (95%) and used without further purification. For *cis-* and *trans*-2-methylvinoxy, the precursor was ethyl 1-propenyl ether, $CH_3CH{=}CHOC_2H_5$, available only as a mixture of the cis and trans forms. Attempts to enhance one isomer over the other by distillation of the precursor mixture are described below.

The spectra were generated in the best yield using a precursor vapor pressure of about 150 Torr (seed ratio 0.1). About 30 mJ/pulse of ArF excimer laser at 193 nm is gently focused to an 8 mm × 4 mm rectangular spot (long side parallel to molecular beam) centered 4 mm downstream of the pulsed nozzle face plate. More intense photolysis destroys the spectra reported here and creates intense spectra due to C_2 and C_3 fragments. Laser-induced fluorescence spectra were excited by a frequency-doubled, tunable dye laser (10 ns fwhm, Lumonics, Hyperdye-300) pumped by the 532 nm harmonic of a Nd:YAG laser (Lumonics, HyperYAG-1200). The laser is collimated to a spot size of 4 mm diameter and positioned 7.0 cm downstream of the nozzle. Unfiltered fluorescence was collected perpendicular to the molecular beam and dye laser axes by an *f*/2 set

---

* To whom correspondence should be sent. E-mail: weisshaar@chem.wisc.edu.

[†] Current address: Innovative Lasers Corporation, 3280 E. Hemisphere Loop, Tucson, AZ 85706.

S1089-5639(98)00451-4 CCC: $15.00

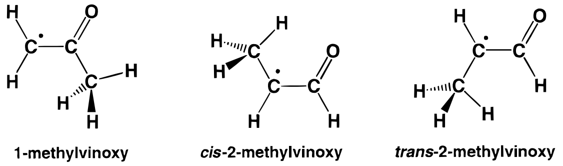

Figure 1. Methylvinoxy isomers in minimum-energy conformations calculated for the ground state with unrestricted Hartree−Fock theory.

of quartz lenses and imaged onto a slit/photomultiplier system. The photomultiplier was model R1477 from Hammamatsu with gain of 2 × 10^6. Dye laser pulse energies were typically 2 mJ/pulse and varied by 30−40% across the spectral range 330−370 nm reported here. The dyes were LDS-750, LDS-698, and DCM. The LIF intensities were linear in dye laser pulse energy under our conditions. The spectra presented below are not corrected for variations in laser intensity. The relative intensities of the stronger bands are reproducible to ±20% from scan to scan but accurate to only ±40%.

The survey LIF spectra reported here were collected at a density of 0.2 cm^{-1} per point. Fluorescence intensity was measured by gated integration of the photomultiplier current and digitized on each shot (Stanford Research Systems, models SR250 and SR245). The 50 ns wide gate was delayed by 55 ns relative to the leading edge of the laser pulse to minimize integration of scattered light while including most of the fluorescence decay curve. Such gating discriminates against bands arising from shorter-lived excited states. We calculate that the sensitivity factor decreases from 1.00 for bands with 1/e fluorescence lifetime τ_f of 190 ns to about 0.83 for τ_f = 130 ns, 0.32 for τ_f = 50 ns, and 0.07 for τ_f = 25 ns. This experimental factor is in addition to the decrease in intensity due to smaller fluorescence quantum yields. Typically 10 laser shots were linearly averaged at each wavelength. On a strong band, some 1000 fluorescence photons are detected within the gate. Spectra were checked for contamination by van der Waals clusters by repeating the experiment using 70:30 Ne−He as buffer gas. No significant change occurred. Warmer spectra could be obtained by slightly increasing the energy of the photolysis laser or by moving it downstream.

Fluorescence lifetimes were obtained by linearly averaging 1024 fluorescence intensity traces in a digital oscilloscope (HP 54504A). A scattered light trace was then obtained by turning off the pulsed nozzle and averaging 1024 more traces. The scattered light trace was digitally subtracted from the fluorescence traces prior to analysis. The resulting fluorescence decays were typically exponential over at least five 1/e decay times. A few traces displayed small-amplitude, long-lived tails. The tails were particularly evident on the weaker fluorescence bands and may result from a weak metastable glow from the source which would not subtract out in our procedure. When analyzed as a sum of two exponentials, even these weaker traces had no more than 0.5% amplitude from the long-lived tail, whose decay time was typically greater than 5 μs. To obtain the lifetimes reported here, we analyzed all traces as a single-exponential decay with variable baseline; i.e., we fit the traces to the function

$$I(t) = A\exp(-k_f t) + B \tag{1}$$

where A, B, and $k_f = \tau_f^{-1}$ are parameters fitted in a least-squares sense. In all cases, the ratio B/A was less than 0.01. In most cases, it was less than 0.006. The lifetimes are estimated accurate to ±10 ns. The very few lifetimes shorter than 50 ns may be less accurate.

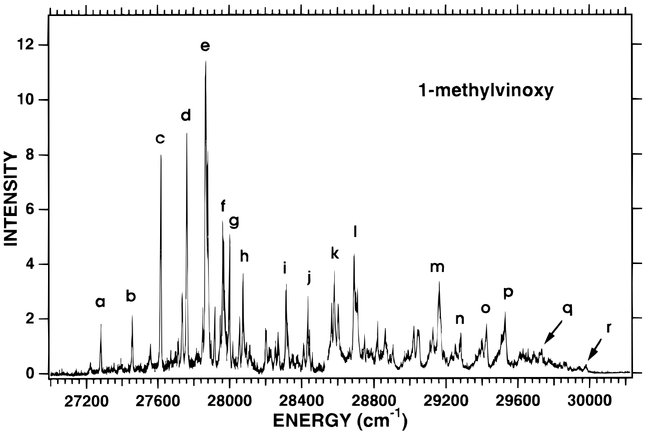

Figure 2. Laser-induced fluorescence spectrum of 1-methylvinoxy.

TABLE 1: $\tilde{B} \leftarrow \tilde{X}$ Laser-Induced Fluorescence Bands and $\tilde{B}$-State Lifetimes of 1-Methylvinoxy

band	energy (cm^{-1})[a]	E_{vib}[a]	lifetime (ns)[b]
a	27 282.7	0.0	111
b	27 459.5	176.8	131
c	27 617.0	334.3	114
d	27 763.0	480.3	120
e	27 870.0	587.3	130
f	27 962.0	679.3	115
g	28 001.4	718.7	105
h	28 075.9	793.2	90
i	28 315.8	1033.1	99
j	28 433.6	1150.9	85
k	28 581.3	1298.6	75
l	28 691.6	1408.9	80
m	29 163.5	1880.8	64
n	29 282.7	2000.0	67
o	29 423.0	2140.3	51
p	29 528.6	2245.9	49
q	29 732.8	2450.1	41
r	29 983.1	2700.4	26

[a] Band intensity peaks, accurate to ±0.5 cm^{-1}; E_{vib} accurate to ±1.0 cm^{-1}. [b] Lifetimes estimated accurate to ±10 ns.

Results

Photolysis at 193 nm of the precursor methyl isopropenyl ether, which has only a single isomer, produces a complex LIF spectrum exhibiting at least 50 bands in the range 27 250−30 000 cm^{-1} (Figure 2). The onset of this spectrum lies some 1500 cm^{-1} to the red of the $\tilde{B} \leftarrow \tilde{X}$ origin in vinoxy inself. Assuming that the same photochemical step (loss of alkyl from the ether) occurs for our precursor as occurs in methyl vinyl ether, we assign the spectrum of Figure 2 to the $\tilde{B} \leftarrow \tilde{X}$ transition in 1-methylvinoxy. The spectrum in Figure 2 shares no bands with vinoxy itself.[12] We scanned 1350 cm^{-1} further to the red and 1000 cm^{-1} further to the blue but found no additional bands. The spectrum is insensitive to buffer gas (changing from Ar to a Ne/He mixture) and to seed ratio, which rules out contributions from van der Waals molecules such as 1-methylvinoxy(Ar)$_x$ and argues against contributions from complexes such as 1-methylvinoxy(precursor)$_x$.

We measured fluorescence lifetimes for the 18 bands labeled a through r in Figure 2. The band intensity maxima, $\tilde{B}$-state vibrational energies (assuming band a is the origin), and fluorescence lifetimes are collected in Table 1. The spectrum perhaps shows evidence of increased bandwidths above E_{vib} = 1400 cm^{-1}, suggesting the onset of strong mixing of torsion−vibrational states, a prelude to rapid intramolecular vibrational redistribution.[19] The fluorescence lifetimes decrease fairly

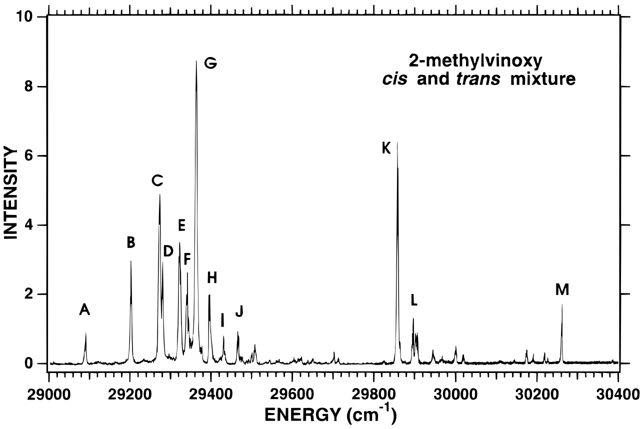

Figure 3. Laser-induced fluorescence spectrum of unknown mixture of *cis*- and *trans*-2-methylvinoxy.

monotonically from 111 to 131 ns near the origin down to 26 ns for band r at $E_{\mathrm{vib}} = 2700$ cm^{-1}.

Photolysis at 193 nm of the precursor molecule ethyl 1-propenyl ether expanded in Ar yields the LIF spectrum shown in Figure 3. We reproducibly observe at least 22 bands beginning at 29 096 cm^{-1}, which is 300 cm^{-1} to the blue of the $\tilde{B} \leftarrow \tilde{X}$ origin of vinoxy itself. Again assuming analogous photochemistry, we assign the spectrum to an unknown mixture of *cis*- and *trans*-2-methylvinoxy radical. We scanned an additional 1300 cm^{-1} to the red and an additional 1200 cm^{-1} to the blue but found no additional bands. Again, the spectrum was insensitive to changes in seed ratio or to switching from Ar to Ne/He buffer gas. The spectrum has no bands in common either with the spectrum in Figure 2 or with the well-known spectrum of vinoxy radical itself.[12]

We attempted to distinguish the spectrum of *cis*-2-methylvinoxy from *trans*-2-methylvinoxy as follows. The precursor arrives as a mixture of approximately 65% cis and 35% trans isomers, as judged by NMR spectral intensities for the neat liquid. Since the cis precursor boils at 69 °C while the trans precursor boils at 75 °C, we were able to partially separate the precursor isomers by distillation. We could create mixtures that varied in cis:trans composition by a factor of 16, from 4:1 to 1:4 as determined by NMR spectra. Moreover, these precursor mixtures were stable on the time scale of our experiment, indicating a large barrier to cis−trans interconversion in the precursor compound. However, within experimental uncertainty, both mixtures produced the same LIF spectrum shown in Figure 3. Evidently, we always obtained the LIF spectrum of the *same* mixture of *cis*- and *trans*-2-methylvinoxy. The fractional contribution of each isomer to the spectrum in Figure 3 is unknown. It appears that, under our photolysis conditions, the cis−trans isomerization of the radical photoproducts is rapid on the time scale of expansion and cooling. This could result from the large internal energy deposited in the nascent radicals, from a small isomerization barrier for the radicals, or from a combination of both effects.

We measured fluorescence lifetimes of 11 of the stronger bands, labeled A through K in Figure 3. The band intensity maxima, vibrational energy within the $\tilde{B}$ state (assuming band A is origin), and the fluorescence lifetimes are collected in Table 2. The lifetime remains fairly constant at 180−190 ns from band A to band H ($E_{\mathrm{vib}} = 0{-}767$ cm^{-1}), decreases substantially for bands I (159 ns) and J (75 ns), and then again increases to 140 ns for band K. Above band K, only one very weak band at 30 385 cm^{-1} is consistently observed. The lifetimes may eventually provide clues to the vibronic assignments.

TABLE 2: $\tilde{B} \leftarrow \tilde{X}$ Laser-Induced Fluorescence Bands and $\tilde{B}$-State Lifetimes of an Unknown Mixture of *cis*- and *trans*-2-Methylvinoxy

bands	energy (cm^{-1})[a]	E_{vib}[a]	lifetime (ns)[b]
A	29 090.1	0.0	191
B	29 202.5	112.4	189
C	29 273.5	183.4	189
D	29 279.5	189.4	
E	29 322.3	232.2	190
F	29 340.5	250.4	190
G	29 363.1	273.0	181
H	29 394.3	304.2	190
I	29 430.0	339.9	
J	29 467.2	377.1	188
K	29 857.7	767.6	159
L	29 895.7	805.6	75
M	30 260.5	1170.4	140

[a] Band intensity peaks, accurate to ±0.5 cm^{-1}; E_{vib} accurate to ±1.0 cm^{-1}. [b] Lifetimes estimated accurate to ±10 ns.

Discussion

The $\tilde{B} \leftarrow \tilde{X}$ spectrum of the vinoxy radical itself has recently been extended and reanalyzed by Brock and Rohlfing.[12] The LIF spectrum begins at 28 784 cm^{-1} and shows substantial activity in several totally symmetric modes including ν_9 (449 cm^{-1}, CCO bend), ν_8 (917 cm^{-1}, CC stretch), and ν_7 (1122 cm^{-1}, CH$_2$ rock). The fluorescence intensity drops precipitously beyond the 5_0^1 band at $E_{\mathrm{vib}} = 1406$ cm^{-1} in the $\tilde{B}$ state. However, both hole-burning[11] and two-color resonant four-wave mixing spectra[12] show that substantial Franck−Condon activity extends over an additional 1800 cm^{-1} to 32 000 cm^{-1} ($E_{\mathrm{vib}} =$ 3200 cm^{-1}). Accordingly, the $\tilde{B}$-state fluorescence lifetime decreases abruptly beyond $E_{\mathrm{vib}} = 1406$ cm^{-1}. The $\tilde{B}$-state decay rate is evidently enhanced by excitation of out-of-plane modes compared with in-plane modes.

On methyl substitution, we find that the single isomer of 1-methylvinoxy (Figure 2) produces a much more complex spectrum than the unknown mixture of cis−trans isomers of 2-methylvinoxy (Figure 3). At the limits of our detection sensitivity, the $\tilde{B} \leftarrow \tilde{X}$ LIF spectrum of the single isomer of 1-methylvinoxy extends over a much wider range (2700 cm^{-1}) than the spectrum of either the mixture of *cis*- and *trans*-2-methylvinoxy (1170 cm^{-1}) or of vinoxy itself (1400 cm^{-1}). The $\tilde{B}$-state lifetimes of 1-methylvinoxy near the origin are significantly shorter (110−130 ns) than those of either the mixture of *cis*- and *trans*-2-methylvinoxy (diminishing from 190 ns near the apparent origin) or of vinoxy itself[12] (diminishing from 190 ns near the origin).

Efforts to assign the new spectra are underway. At present, we have made better progress in assigning the spectrum of the single isomer, 1-methylvinoxy (Figure 2), despite its seemingly greater complexity. The peaks labeled a−f can be fit both in frequency and in intensity using a one-dimensional model of methyl torsion.[20] The a−b−c−d−e−f pattern of frequency intervals can be found at least three more times in the spectrum, built atop vibrational intervals of 452, 820, and 1659 cm^{-1}. The first two of these intervals roughly match the active 9_0^1 and 8_0^1 bands at 449 and 917 cm^{-1} in the spectrum of vinoxy itself. The third interval is likely the carbonyl stretch ν_4', whose frequency is 1621 cm^{-1} in the $\tilde{B}$ state of vinoxy. The 4_0^1 band is very weak in the LIF spectrum of vinoxy, not for lack of Franck−Condon factor, but because it lies above the onset of fast $\tilde{B}$-state decay. In changing from vinoxy to 1-methylvinoxy, each intense vibronic band makes a 7−8-member progression in the methyl torsional mode, resulting in the large number of bands observed.

The unusual a−b−c−d−e−f intensity pattern and rapidly converging level structure clearly signal a 180° change from the $\tilde{X}$ to the $\tilde{B}$ state in the torsional angle at the potential minimum for methyl rotation. In addition, the barrier to methyl group internal rotation must be very large in the $\tilde{B}$ state, approximately 750 cm^{-1}. The spectrum does not constrain the ground-state barrier, except that it must be large enough to localize the wave function in the well. Our preliminary single-configuration ab initio calculations[21] suggest that the barrier to methyl rotation in the ground state of 1-methylvinoxy is small, roughly 70 cm^{-1}, but the accuracy of that level of theory for radical barriers is not yet known. The calculated potential minimum for the ground state places one CH bond in the plane of the CCO frame cis to the CO bond. Thus, we tentatively infer that the $\tilde{B}$-state minimum places one CH bond cis to the CC bond of the CCO frame.

The underlying reason for the large $\tilde{B}$-state barrier is not yet clear. It is probably closely related to the large geometry change in the CCO frame on $\tilde{B} \leftarrow \tilde{X}$ excitation and the concomitant change in π-bond order of the CC and CO bonds vicinal to the methyl CH bonds. In earlier work,[16] we were able to understand such effects in substituted toluenes in great detail. The methyl barrier height correlates with the calculated difference in bond order between the pair of ring CC bonds vicinal to the methyl CH bonds. The methyl prefers to lie with one CH cis to the CC bond of higher order. The analogous vicinal bonds in 1-methylvinoxy are the frame CC and CO bonds. The structure of ground-state vinoxy is closer to the $\dot{C}H_2{-}CHO$ carbonyl structures of Figure 1 than to the oxy radical structure $CH_2{=}CH\dot{O}$.[22] One simple picture of the $\tilde{B} \leftarrow \tilde{X}$ transition consistent with the A″ symmetry of the $\tilde{B}$ state and roughly consistent with the lengthening of the carbonyl bond in vinoxy is a $\pi^* \leftarrow \pi$ transition on the carbonyl group. In this view, the methyl group in the $\tilde{B}$ state of 1-methylvinoxy sees a diradical on the carbonyl side (broken π bond) and substantial remaining double-bond character on the CC side of the frame. While this begins to explain the strong preference in the $\tilde{B}$ state for the methyl conformation with CH bond cis to the CC bond of the frame, the 750 cm^{-1} magnitude of the $\tilde{B}$-state barrier is surprisingly large.

In the spectrum of the mixed *cis*- and *trans*-2-methylvinoxy sample, we have not yet found a one-dimensional methyl torsional model that fits the bands A, B, C, D, E, G, and I. Nor does that pattern obviously reproduce itself elsewhere in the spectrum. Successful modeling of the spectrum may require information about both the cis−trans barrier height and the barrier to internal methyl rotation in both the $\tilde{X}$ and $\tilde{B}$ states. If these two motions interact strongly, analysis using simple standard spectroscopic models may fail.

The new spectra have already proven useful as fingerprints for confirming the identity of chemical reaction products. Very recently, Bersohn and co-workers[13] have been studying the reaction mechanism of $O(^3P)$ with a variety of alkyl-substituted alkenes. From $O(^3P)$ + isobutene, they observed what is unmistakably a hotter version of the spectrum of Figure 3. The present work confirms the identity of the product as 2-methylvinoxy. This is consistent with initial attack by $O(^3P)$ on the $=CH_2$ end of isobutene to form the triplet diradical $(CH_3)_2{-}\dot{C}{-}CH_2\dot{O}$, which loses H directly on the triplet surface to form 2,2-dimethylvinoxy or undergoes intersystem crossing to the lower energy singlet surface. The singlet diradical undergoes a facile 1,2-hydrogen shift to form the hot aldehyde $(CH_3)_2$-$CH{-}CHO$, which subsequently loses methyl to form 2-methylvinoxy. Both H atom loss (presumably to form 2,2-dimethylvinoxy) and now the 2-methylvinoxy channel have been directly observed by Bersohn. The *absence* of the spectrum from 1-methylvinoxy indicates that the analogous displacement of a *methyl* group on the triplet surface by attack of $O(^3P)$ on the $(CH_3)_2{=}$ side of isobutene does not compete effectively.

In other work, Washida and co-workers[14] recently detected a hotter version of the LIF spectrum of 1-methylvinoxy (Figure 2). Their spectrum arose from the reaction $F + (CH_3)_2CO \rightarrow$ 1-methylvinoxy + HF in a microwave discharge apparatus. In the future, it could prove useful to obtain the jet-cooled spectrum of a variety of disubstituted and even trisubstituted vinoxy radicals to further assist in identification of complex chemical reaction products.

Finally, we comment on the effects of methyl substitution on the $\tilde{B}$-state dynamics and the threshold for rapid nonradiative decay. In simple vinoxy, Neumark and co-workers[17] have shown that photodissociation to a mixture of CH_3 and CO fragments occurs even at the $\tilde{B}$-state origin. They also detect the $H + CH_2CO$ channel following excitation to bands above 1400 cm^{-1}, where the ratio of $CH_3 + CO$ to $H + CH_2CO$ fragment yields is about 1:4. On the basis of ab initio calculations,[22] they suggest that the sharp decrease in lifetime near 1400 cm^{-1} arises from the onset of fast nonradiative decay enhanced by a surface intersection between twisted forms of the $\tilde{B}$ state and either the $\tilde{A}$ state or the $\tilde{C}$ state. The softness of the out-of-plane twisting motion in the $\tilde{B}$ state ($\nu_{12}' = 274$ cm^{-1}) may help the surface intersection to occur at relatively low excitation energies.

In all three molecules, vinoxy, 1-methylvinoxy, and 2-methylvinoxy, the $\tilde{B} \leftarrow \tilde{X}$ spectrum exhibits a similar abrupt cutoff in LIF intensity and sharp decrease in fluorescence lifetime. Interestingly, the onset of fast decay occurs in a very narrow range of *total* excitation energy in all three molecules, 29 900−30 200 cm^{-1}. When measured in terms of E_{vib} within the $\tilde{B}$ state, the onset of fast decay occurs over a much wider range of energies, 1400 cm^{-1} in vinoxy, 1200 cm^{-1} in 2-methylvinoxy, and 2700 cm^{-1} in 1-methylvinoxy. Perhaps the role of methyl substitution is merely to shift the relative electronic energies of two interacting states, such as the $\tilde{B}$ and $\tilde{A}$, and thus the energy of a key surface intersection. That seems possible in view of the substantial 1500 cm^{-1} shift in $\tilde{B} \leftarrow \tilde{X}$ origin from vinoxy to 1-methylvinoxy. Alternatively, fast intramolecular vibrational energy redistribution within the $\tilde{B}$ state to vibrational states rich in methyl rotation might *delay* the onset of fast electronic relaxation by draining internal energy away from the modes that promote interelectronic conversion. A third possibility worth considering is that the fast decay signals the onset of photodissociation to the *triplet* ketene channel. In vinoxy itself, the ab initio calculations place H + triplet ketene within 0.15 eV of the onset of fast $\tilde{B}$-state decay. This channel would likely go undetected in Neumark's photodissociation fragment imaging experiment, since the recoil energy would be very small and the lighter H atoms are intrinsically difficult to detect. It might be interesting to search for slow $CH_2CO + CH_3$ fragments from 1-methylvinoxy photodissociation below and above 29 800 cm^{-1}.

Acknowledgment. We thank the U.S. Department of Energy, Chemical Sciences Division, Office of Basic Energy Sciences, for generous support of this research under Contract DE-FG02-92ER14306.

References and Notes

(1) Schmoltner, A. M.; Chu, P. M.; Brudzynski, R. J.; Lee, Y. T. *J. Chem. Phys.* **1989**, *91*, 6926.

(2) *Combustion Chemistry*; Gardiner, W. C., Jr., Ed.; Springer-Verlag: New York, 1984.

(3) Hucknall, D. J. *Chemistry of Hydrocarbon Combustion*; Chapman and Hall: London, 1985.

(4) Cvetanovic, R. J.; Singleton, D. L. *Rev. Chem. Intermed.* **1984**, *5*, 183.

(5) Ramsay, D. A. *J. Chem. Phys.* **1965**, *43*, 518.

(6) Gutman, D.; Nelson, H. H. *J. Phys. Chem.* **1983**, *87*, 3902.

(7) Donaldson, D. J.; Okuda, I. V.; Sloan, J. J. *Chem. Phys.* **1995**, *193*, 37.

(8) Inoue, G.; Akimoto, H. *J. Chem. Phys.* **1981**, *74*, 425.

(9) DiMauro, L. F.; Heaven, M.; Miller, T. A. *J. Chem. Phys.* **1984**, *81*, 2339.

(10) Wan, R.; Chen, X.; Wu, F.; Weiner, B. R. *Chem. Phys. Lett.* **1996**, *260*, 539.

(11) Gejo, T.; Takayanagi, M.; Kono, T.; Hahazaki, I. *Chem. Lett.* **1993**, 2065.

(12) Brock, L. R.; Rohlfing, E. A. *J. Chem. Phys.* **1997**, *106*, 10048.

(13) Quandt, R.; Min, Z.; Wang, X.; Bersohn, R. *J. Phys. Chem. A* **1998**, *102*, 60.

(14) Washida, N.; Inomata, S.; Furubayashi, M., work in progress.

(15) Kiefer, J. H.; Mudipalli, P. S.; Wagner, A. F.; Harding, L. B. *J. Chem. Phys.* **1996**, *105*, 8075.

(16) Lu, K. T.; Weinhold, F.; Weisshaar, J. C. *J. Chem. Phys.* **1995**, *102*, 6787.

(17) Osborn, D. L.; Choi, H.; Mordaunt, D. H.; Bise, R. T.; Neumark, D. M. *J. Chem. Phys.* **1997**, *106*, 3049.

(18) Eiden, G. C.; Lu, K.-T.; Weisshaar, J. C. *J. Chem. Phys.* **1996**, *104*, 8886.

(19) Moss, D. B.; Parmenter, C. S. *J. Chem. Phys.* **1993**, *98*, 6897.

(20) Breen, P. J.; Warren, J. A.; Bernstein, E. R.; Seeman, J. I. *J. Chem. Phys.* **1987**, *87*, 1917.

(21) Williams, S.; Weisshaar, J., work in progress. For the ground state of 1-methylvinoxy, the calculated vibrationally adiabatic methyl torsional barrier is 66 cm^{-1} at the UHF/6-31G(d) level of theory and 68 cm^{-1} at the UHF/6-311+G(d,p) level, with no correction for differential zero-point effects. The minimum places one CH bond of methyl cis to the CO bond of the CCO frame, as shown in Figure 1.

(22) Yamaguchi, M. *Chem. Phys. Lett.* **1994**, *221*, 531.