JOURNAL OF CHEMICAL PHYSICS VOLUME 115, NUMBER 1 1 JULY 2001

# Vibrational state distribution and relaxation of vinoxy radicals

Hongmei Su and Richard Bersohn[a)]
*Department of Chemistry, Columbia University, New York, New York 10027*

(Received 24 January 2001; accepted 13 March 2001)

The vinoxy radical $\cdot CH_2CHO$ is a product of the reaction of $O(^3P)$ atoms with terminal alkenes and can also be made by photodissociation of an alkyl vinyl ether. In either case it is formed in a vibrationally excited state. The nascent radical displays a rich electronic spectrum to the red of its $X \rightarrow B$ band origin consisting of bands originating from vibrationally excited states. Some transitions, true ''hot bands,'' terminate on the vibrationless $B$ state; others, sequence bands, terminate on vibrationally excited $B$ states. The spectra become unobservably weak at a certain energy. The difference between that energy and the energy of the band origin is roughly the maximum vibrational energy in the radical. This is 5600 $cm^{-1}$ for the vinoxy produced by photodissociation of ethyl vinyl ether at 193 nm and 3200 $cm^{-1}$ for the product of the reaction of $O(^3P)$ with ethylene, propene, 1-butene, and 1-pentene. There is a remarkable cooling of the vibrations as the hydrocarbon chain lengthens. The average vibrational energy of the vinoxy product of the reaction $O(^3P)$ with ethylene, propene, 1-butene, and 1-pentene is 2100, 1800, 1570, and 1180 $cm^{-1}$, respectively. This cooling implies that the reaction complex lives long enough for internal vibrational relaxation to occur. The average vibrational energy in the reaction-produced vinoxy is small, which implies that there is considerable kinetic energy. The time dependence of the intensity of the hot bands measures the relaxation rates of different energies, some of which are the energies of a single vibrational state. The ground-state population increases monotonically to an asymptote. The population of most states grows with time and then decays. The growth is due to a cascading from upper states. The populations of the highest energy states decay monotonically; the still higher energy states are almost unpopulated. These results prove that the relaxation proceeds stepwise. The magnitude of the step, ~200–300 $cm^{-1}$, can be inferred from the growth rate of the ground-state population.
[DOI: 10.1063/1.1369602]

## I. INTRODUCTION

The vinoxy radical, $\cdot CH_2{-}CH{=}O$, is a product of the reaction of $O(^3P)$ with terminal alkenes

$$O(^3P) + RCH{=}CH_2 \rightarrow R\cdot + \cdot CH_2{-}C{=}O. \quad (1)$$

It can also be prepared by photodissociation of an alkyl vinyl ether

$$R{-}O{-}CH{=}CH_2 + h\nu \rightarrow R\cdot + \cdot CH_2{-}CH{=}O. \quad (2)$$

The electronic and microwave spectroscopies of vinoxy have been extensively investigated.[1–3] Three electronic states have been identified in this planar molecule, the ground state $\tilde{X}\ ^2A''$, an $\tilde{A}\,^2A'$ state at ~8000 $cm^{-1}$, and a $\tilde{B}\,^2A''$ state whose origin is at 28 785.8 $cm^{-1}$. The vibrational frequencies and structures are known in both the $\tilde{X}$ and the $\tilde{B}$ states. Because the ground-state wave function is odd with respect to reflection in the molecular plane, the unpaired electron must be in a $\Pi$ state. There are two valence bond structures possible: $\cdot CH_2{-}CH{=}O$, formyl methyl, and $CH_2{=}CH{-}O\cdot$, vinoxy. The first structure is favored by the finding through microwave spectroscopy that the unpaired spin density is largest on the methylene carbon atom. Additional evidence that the ground-state structure is mainly formyl methyl is furnished by a comparison of the rates of reaction of $O_2$ with methoxyl and vinoxy.[4] Vinoxy reacts two orders of magnitude faster than methoxyl. If the spin density of vinoxy were mainly on the oxygen atom as in methoxyl, the rate constants would have been similar. On the other hand, the C=O bond distance in vinoxy is 0.05 Å longer than in acetaldehyde, suggesting that the C=O bond in vinoxy is not a pure double bond.[5]

Fortunately, vinoxy is brightly fluorescent when excited at its $0_0^0$ transition (3.57 eV). It is not obvious that this should be so because the energy required to dissociate vinoxy into $CH_3 + CO$ is only $0.08 \pm 0.09$ eV. Only $1.49 \pm 0.09$ eV are required to form $H + CH_2{=}C{=}O$. Both channels are observed in very low yield when vinoxy is excited at the band origin, but in high yield at excitation 1600 $cm^{-1}$ above the band origin.[6] The clue to the explanation for the fluorescence may be the fact that when vinoxy is excited in the $\tilde{X} \rightarrow \tilde{B} 0_o^0$ band most of the emission is considerably redshifted (see Fig. 1). The large difference in structure between the ground- and excited state traps the excited molecule long enough that it can radiate. The vibrationless $B$ state has a fluorescence lifetime of 190 ns.[2]

The dispersed fluorescence spectrum of vinoxy excited at the band origin (reproduced from Ref. 2) is shown in

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[a)] Electronic mail: rb18@columbia.edu

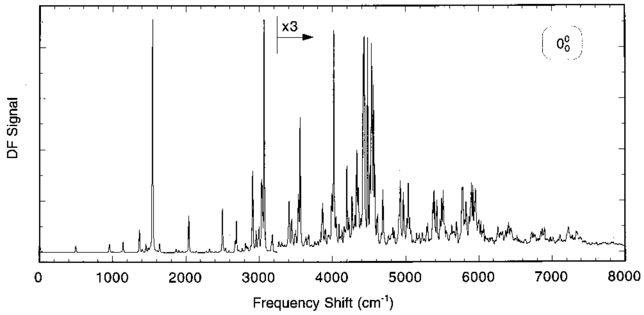

FIG. 1. Dispersed fluorescence spectrum of jet-cooled vinoxy excited at the band origin (reproduced from Ref. 2 with permission).

Fig. 1. All the emission is from the single lowest $\tilde{B}$ state with a single lifetime of 190 ns. As the ground-state energy increases the number of quanta increases; the density of states increases rapidly but the Franck–Condon (F–C) factors decrease even more rapidly. The spectrum cuts off at about 7500 $cm^{-1}$. There is an essential difference between the emission spectrum of Fig. 1 and the other spectra in this paper which are all LIF excitation spectra. The intensity of the lines in the emission spectrum is proportional to their F–C factors. The excitation spectra are basically absorption spectra and their intensities are proportional to a product of a F–C factor and the population of the lower energy state.

We and others have noticed that when vinoxy is produced by photodissociation, fluorescence intensity is increased with increasing delay time between the pump and probe laser pulses.[7–9] The implication is that some sort of relaxation process is increasing the population of the ground vibrational state. For this reason many experiments on vinoxy radical are conducted 50–100 $\mu$s after the initial formation of vinoxy in order to obtain a complete vibrational relaxation and a maximum absorption at 347.4 nm.

The goal of the present paper is twofold. One is to measure, as far as possible, the nascent vibrational distribution in vinoxy, both as a photofragment and a reaction product. The second is to measure the rates of vibrational relaxation of vinoxy radicals.

Vinoxy radical was generated by 193 nm photodissociation of either methyl or ethyl vinyl ether (EVE). There was negligible difference between spectra derived from the two sources, and EVE was somewhat more convenient to use. The laser-induced fluorescence (LIF) excitation spectra of vinoxy were measured at a pressure of 40 millitorr and a time delay of 2 $\mu$s. This time delay was necessary to permit the photomultiplier tube (PMT) to recover from the strong fluorescence generated by the 193 nm light. Relaxation studies were carried out at a pressure of 300 millitorr, 40 millitorr of the vinyl ether and the balance due to the buffer gas. Reaction-produced vinoxy was studied using a mixture of $SO_2$ (100 millitorr) and hydrocarbon (200 millitorr). A 2 $\mu$s delay was used, this time in order to allow enough reactive collisions to produce sufficient vinoxy for detection.

Relaxation measurements were carried out by measuring the LIF intensity at a particular excitation energy as a function of time starting 2 $\mu$s after the formation of the radicals. The usual pressure of the buffer gas was 300 millitorr. This had to be increased for the inefficient diatomic relaxers $O_2$ and $N_2$. Doubling the pressure resulted in a shortening of the rise time and the fall time of the signal by a factor of 2. Effort was expended on obtaining rate constants with a variety of gases rather than obtaining very precise values of any one of them.

## II. EXPERIMENT

All experiments were carried out in an 8 cm cube through which a gas flowed. The dissociating and exciting light beams entered opposite windows of the cube. The vinoxy radicals were generated by reaction of $O(^3P)$ atoms with a terminal alkene or by photodissociating at 193 nm methyl or ethyl vinyl ether. The ethyl compound is slightly preferable because there is somewhat weaker emission generated through multiphoton processes by the strong 193 nm laser (Lambda Physik Compex 102). This emission is not seen in the reactions, so the emitting source must be a fragment of the ether or of vinoxy. In other experiments the same laser was used to generate $O(^3P)$ atoms by dissociating $SO_2$. Fluorescence of vinoxy was excited by a dye laser pumped by a XeCl laser (Lambda Physik, LPX 300). The dyes DMQ, BBQ, DPS, and Stilbene 420 were used for the ranges 347 to 372 nm, 367 to 396 nm, 399 to 415 nm, and 420 to 440 nm, respectively. Two long-pass filters at 350 and 365 nm were used with the DMQ dye, a long-pass filter at 420 nm with DPS, and a long-pass filter at 440 nm with the Stilbene 420. Mounted on top of the cube was a tube containing a lens which focused the fluorescent light onto a photomultiplier (PMT). The photomultiplier output was amplified and then entered a gated integrator (Stanford Research). The signal from the latter was digitized by a Keithley KPCI-3101 card inside of a PC. Hot bands were also sought using cavity ring-down spectroscopy, but because of the long times required by this technique only the band origin could be detected.

## III. RESULTS AND DISCUSSION

### A. LIF excitation spectrum of the vinoxy photoproduct

When methyl vinyl ether absorbs one photon at 193 nm, two pathways for dissociation suggest themselves

$$CH_3\text{–}O\text{–}CH{=\!=}CH_2 + h\nu(193\,\text{nm}) \rightarrow \cdot CH_2\text{–}CH{=\!=}O + \cdot CH_3, \tag{3}$$

$$CH_3\text{–}O\text{–}CH{=\!=}CH_2 + h\nu(193\,\text{nm}) \rightarrow CH_3O\cdot + CH_2\text{–}CH\cdot. \tag{4}$$

Using the following heats of formation (in kJ/mol) of the radicals $CH_3(146.4)$, $CH_2\text{–}CH{=}O(10.5\pm9.2)$, $CH_2\text{–}CH(117.0\pm4.2)$, and $CH_3O(14.6)$, one finds that the channel of Eq. (4) requires $25.5\pm10.1\,\text{kJ mol}^{-1}$ less energy than the channel of Eq. (3), with which we are concerned.[10] The absolute energy required for the two dissociation channels depends on the enthalpy of formation of methyl vinyl ether. This is not known but can be estimated as the average of the heats of formation of dimethyl ether ($-184.1$) and divinyl ether ($-13.6\pm4.0$) which is $-98.9\pm4.0\,\text{kJ mol}^{-1}$.[11] Using 193 nm photons the available energy for reaction (3) is 366.4 kJ or 30 600 $cm^{-1}$.

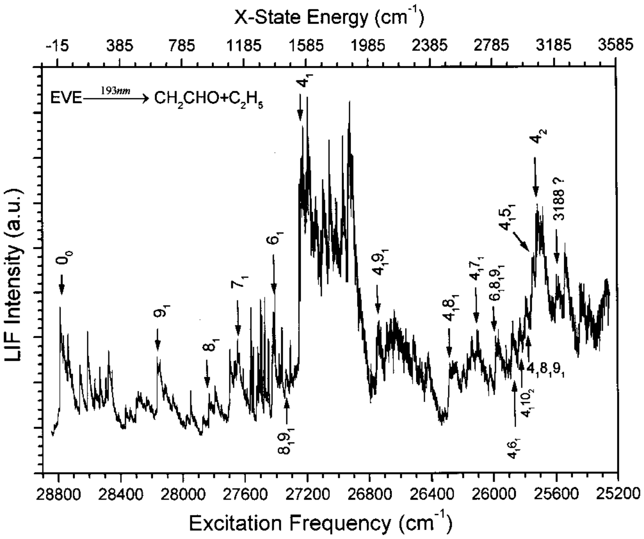

FIG. 2. Redshifted LIF excitation spectrum of vinoxy photoproduct of methyl vinyl ether irradiated at 193 nm. The spectra are in the energy range 0 to 3580 cm$^{-1}$.

The rich and complex spectrum of vinoxy photodissociated from EVE extends from the band origin to the red out to 5620 cm$^{-1}$. The spectrum shown in Figs. 2, 3, and 4 was divided into four spectral ranges. Each range was obtained with a different dye, therefore, adjacent spectra can only be compared with each other if a specific band is common to both. To save space the spectra have been combined into two plots. The actual resolution is better than that shown in Fig. 2. The spectrum was taken at 40 millitorr pressure with a 2 $\mu$s delay. At low energies the peaks can be identified as arising from singly excited specific vibrational states. The strongest bands are the origin and the $4_1^0$ and $4_2^0$ bands. The individual intensities are proportional to the product of their F–C factor and the population of the initially vibrationally excited state. Fortunately, the relative F–C factors may be obtained from the dispersed fluorescence spectrum of jet-cooled vinoxy excited at the electronic origin shown in Fig. 1.[2] Brock and Rohlfing were able to identify 57 ground vibrational states, most with small F–C factors. The third column of Table I (supplied by Eric Rohlfing) is a list of relative F–C factors for those bands in our spectra which we could assign. These intensities may be taken as proportional to the F–C factors for these transitions. The F–C factors have also been calculated theoretically by Yamaguchi *et al.*[9,12] This is a difficult calculation because of the relatively large differences in bond lengths between the ground- and excited states leading to extensive mixing of modes, and there are substantial differences between the theoretical and experimentally determined F–C factors obtained by Brock and Rohlfing which are listed in Table I. The latter have been used in the interpretation of our spectra.

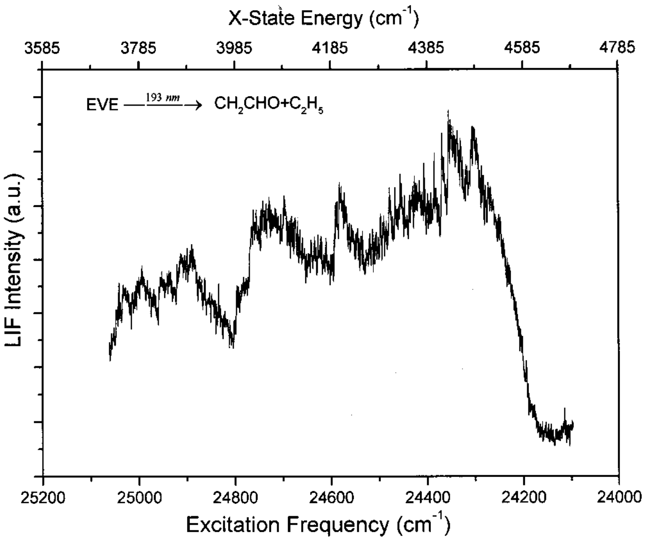

FIG. 3. Same as Fig. 2 for redshifts 3580 to 4780 cm$^{-1}$.

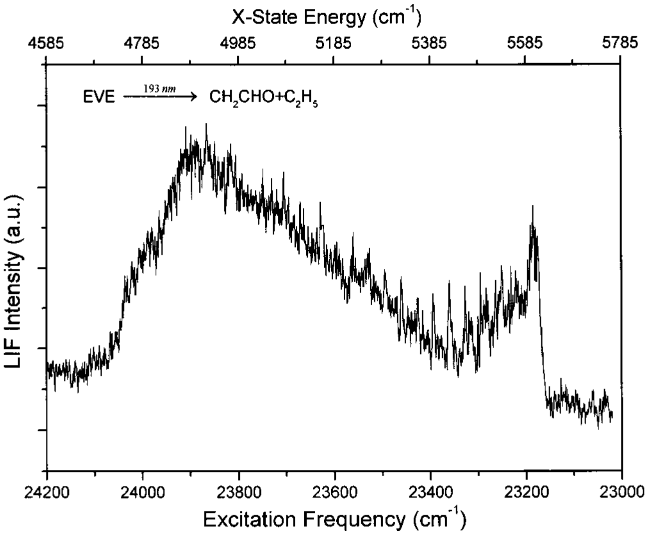

FIG. 4. Same as Fig. 2 for redshifts 4590 to 5780 cm$^{-1}$.

In addition to all the hot bands whose transitions begin on vibrationally excited states and end on the vibrationless *B* state, there is an array of sequence bands which begins on

TABLE I. Vibrational states, energies, relative F–C factors and populations of vinoxy product of reactions of O($^3P$) atoms with terminal alkenes.

| State | Energy (cm$^{-1}$) | Relative F–C factor | Ethene reaction | Propene reaction | 1-butene reaction | 1-pentene reaction |
|---|---|---|---|---|---|---|
| $O_0$ | 0 | 22.7 | 0.03 | 0.04 | 0.07 | 0.12 |
| $9_1$ | 500 | 3.3 | 0.08 | 0.12 | 0.15 | 0.21 |
| $8_1$ | 957 | 3.7 | 0.08 | 0.11 | 0.12 | 0.11 |
| $7_1$ | 1143 | 4.8 | 0.07 | 0.14 | 0.13 | 0.24 |
| $6_1$ | 1366 | 10.0 | 0.05 | 0.05 | 0.07 | 0.05 |
| $8_19_1$ | 1454 | 3.6 | 0.09 | 0.10 | 0.11 | 0.09 |
| $4_1$ | 1543 | 100.0 | 0.01 | 0.01 | 0.02 | 0.01 |
| $4_19_1$ | 2038 | 15.1 | 0.02 | 0.01 | 0.01 | 0.01 |
| $4_18_1$ | 2498 | 16.6 | 0.03 | 0.02 | 0.02 | 0.01 |
| $4_17_1$ | 2688 | 11.8 | 0.11 | 0.10 | 0.07 | 0.03 |
| $6_18_19_1$ | 2813 | 3.5 | 0.11 | 0.06 | 0.06 | 0.03 |
| $4_16_1$ | 2910 | 28.7 | 0.02 | 0.02 | 0.01 | 0.01 |
| $4_110_2$ | 2956 | 7.5 | 0.07 | 0.06 | 0.04 | 0.02 |
| $4_18_19_1$ | 2996 | 9.2 | 0.07 | 0.06 | 0.04 | 0.02 |
| $4_15_1$ | 3034 | 27.1 | 0.04 | 0.02 | 0.02 | 0.01 |
| $4_2$ | 3066 | 84.0 | 0.01 | 0.01 | 0.01 | 0.00 |
| ? | 3188 | 6.3 | 0.10 | 0.08 | 0.05 | 0.04 |

excited vibrational *X* states and ends on vibrationally excited *B* states. These transitions were previously seen and some were assigned by Loison *et al.*[13]

### B. Vibrational distribution of the vinoxy photoproduct

Relaxation studies were carried out on the vinoxy made by photodissociation of alkyl vinyl ethers. There are three reasons for this choice. First, the absolute yield of vinoxy from photodissociation is higher than that from reactions. Second, because the photofragments have much higher internal energy, relaxation rates can be measured at much higher energies. Finally, it would be awkward to interpret the time dependence of an LIF signal of a reaction product. The signal would be increasing in part because more hot vinoxys are being made by reaction and in part by relaxation from still higher levels. The drawback of the use of the photofragments is that a minimum time delay of 2 $\mu$s was necessary because of the bright emission, probably from C–H which covered the same spectral region as the vinoxy emission.

The first absorption band of a molecule $R_1OR_2$ results from the promotion of a nonbonding electron largely in the $O2p\Pi$ state to a $3s$ Rydberg state. This is true provided the R groups are H atoms or saturated alkyl radicals. If, however, one or both R groups are unsaturated, there will be a lower energy transition localized in the unsaturated group.[10,14] Accompanying this absorption there are, as illustrated by Eqs. (3) and (4), two obvious dissociation channels, $R_1O\cdot + R_2\cdot$ and $R_1\cdot$ and $\cdot OR_2$. Measurement of the relative yields is outside the scope of the present paper. We speculate that the vinoxy+alkyl channel probably dominates because the excitation is not primarily a Rydberg transition on the oxygen atom but a $\pi \rightarrow \pi^*$ valence transition within the vinoxy moiety.

The LIF excitation spectrum extends from the band origin at 28 785.8 $\text{cm}^{-1}$ to $\sim$5600 $\text{cm}^{-1}$ lower energy. Because of the presence of sequence bands which could originate from still higher energies, and because of the necessary 2 $\mu$s delay before probing, the populated states might extend 500 to 1000 $\text{cm}^{-1}$ higher but not more than that. This is because sequence bands ending at energies higher than about 1600 $\text{cm}^{-1}$ will not be detected because the upper state dissociates before it can radiate. Also, we know the relaxation rates and calculate that the relaxation in the first 2 $\mu$s does not alter the general trends. The maximum fraction of available energy released as vibrational energy of the vinoxy was $f_V = 5620/30\,600 = 0.18$. The value averaged over the vibrational distribution, $\langle f_V \rangle$, is hard to determine accurately but as discussed below is surely much lower.

The photodissociation of methyl vinyl ether in a molecular beam has recently been studied by Morton *et al.*[15] Their central finding is that the recoil kinetic energy distribution for $O-CH_3$ fission is bimodal. The minor channel ($<10\%$) has an average recoil kinetic energy of 18 500 $\text{cm}^{-1}$. Assuming that the methyl product of this minor channel does not receive much internal energy, the vinoxy product of this channel would have an average internal energy of 11 700 $\text{cm}^{-1}$. The major channel ($>90\%$) has a much smaller average kinetic energy of 4650 $\text{cm}^{-1}$. They interpret this to mean that the vinoxys in the major channel are produced in the *A* state, the first excited electronic state.

There is not necessarily a contradiction between their results on the translational energy distribution and ours on the vibrational energy distribution. In the 2 $\mu$s delay in the present experiments the vinoxys in the *A* state may have lost part of their energy by radiation. Also, as shown in Fig. 1 hot bands originating from vibrational energies exceeding 7500 $\text{cm}^{-1}$ are too weak to be detected. Moreover, the long wavelength bandpass filters which we use eliminate wavelengths shorter than the probe length, thus, as the energy, i.e., the redshift increases, the method becomes progressively less sensitive. Finally, obviously vinoxys in the *A* state would fall apart when excited and not fluoresce. In conclusion, some vinoxys with a large amount of internal energy may have been missed but most vinoxys photoproduced at 193 nm have considerably less than 8000 $\text{cm}^{-1}$ of internal energy.

### C. Relaxation of vinoxy by buffer gas collisions

The time dependence of the hot band LIF signals fall into three categories. The ground-state intensity rises monotonically. The intensities originating from states within 500 $\text{cm}^{-1}$ of the highest occupied state decay monotonically to unobservably low values. The intensities originating from the majority of the occupied states extending from 500 to 5000 $\text{cm}^{-1}$ exhibit a rise and then a fall to asymptotic values which are essentially zero except for the state singly excited in $\nu_9$ at 500 $\text{cm}^{-1}$, which at room temperature has a thermal population of 8%. The ground-state population is still growing after some highly excited states have lost all population. Moreover, the decay of the intensity of the 500 $\text{cm}^{-1}$ line is on the same time scale as the growth of the ground-state population. Clearly, much of the overall relaxation process is via the state with 500 $\text{cm}^{-1}$ energy. The curves shown in Fig. 5 with $SF_6$ as a relaxing gas are similar in general shape to those of all the other relaxing gases. This general behavior is explained by the assumption that vibrational relaxation is a stepwise process involving only small energy changes in each inelastic collision. The rate constants for relaxation of vinoxy by $O_2$ or $N_2$ are an order of magnitude larger than the rate constant for reaction of vinoxy with $O_2$. It follows that in air combustion $O_2$ reacts with equilibrated vinoxys.

Two types of information can be derived from the LIF spectra. The decaying part of the time dependence can be fitted with a decay rate constant which is equal to $kn$, where $k$ is the bimolecular rate constant for vibrational relaxation and $n$ is the number density of the buffer gas. The relaxation rate caused by the undissociated alkyl vinyl ether itself is ignored because its pressure is much lower than that of the relaxing gas. The rate constants for the six different relaxing gases, ethane, methane, sulfur hexafluoride, carbon dioxide, oxygen, and nitrogen are given in Table II. A comprehensive view is thus obtained of relaxation rates as a function of vibrational state and nature of the buffer gas. They are largest for the radicals which have the highest vibrational energy. The rate constants increase with increasing size and number of modes of the buffer gas. The rate constants for each buffer gas increase roughly linearly with the energy. At the highest energy the rate constants are close to gas kinetic,

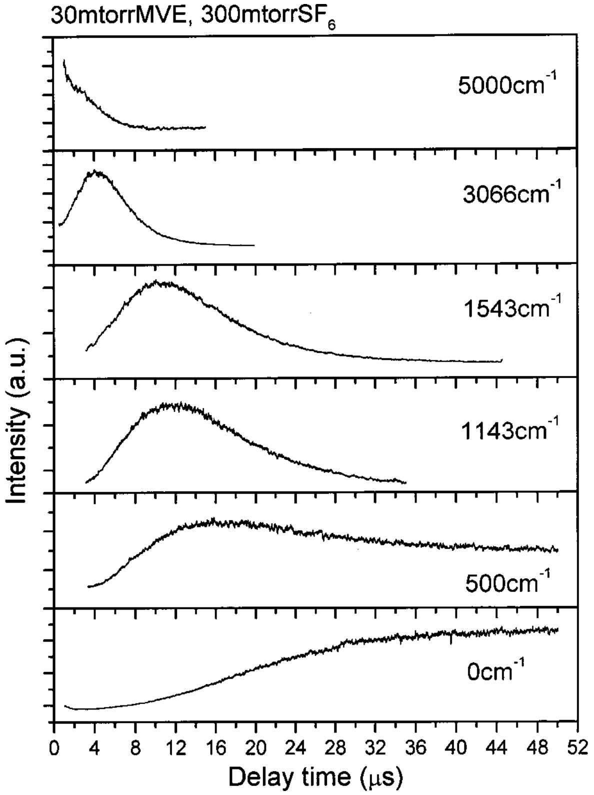

FIG. 5. LIF excitation intensities of vinoxy at different vibrational energies as a function of the time delay between the photodissociation laser and the probing laser.

i.e., almost $10^{-10}\,\mathrm{cm}^3\,\mathrm{mol}^{-1}\,\mathrm{s}^{-1}$. Moreover, the differences in rate constants between the different buffer gases decrease substantially with increasing energy.

What do we learn from these data? First of all, the rise with time of the population of the intermediate states proves that the relaxation is stepwise. If all excited states decayed directly to the ground state, there would be no transient rise in intensity. The monotonic decrease with time of the intensity from the very high energy states is a consequence of the fact that there is relatively little population of still higher states which could increase their population. The relatively large monotonic rise of the intensity of the ground state shows that the initial vibrational distribution was inverted with respect to the ground state.

TABLE II. Relaxation rate constants of vinoxy by buffer gases at different energies. Relaxation rate constants are in units of $10^{-12}\,\mathrm{cm}^3\,\mathrm{molec}^{-1}\,\mathrm{s}^{-1}$. Standard deviation of exponential fit was <1% except for the smallest rate constants.

| Energy ($\mathrm{cm}^{-1}$) | $C_2H_6$ | $SF_6$ | $CH_4$ | $CO_2$ | $N_2$ | $O_2$ |
|---|---|---|---|---|---|---|
| 5000 | --- | 53.8 | --- | --- | --- | --- |
| 4569 | --- | 50.6 | --- | --- | --- | --- |
| 3066 | 38.3 | 33.1 | 26.7 | 23.3 | 13.5 | 12.4 |
| 1543 | 17.4 | 15.3 | 12.5 | 9.2 | 2.9 | 3.0 |
| 1366 | 19.8 | 12.8 | 17.3 | 8.1 | 5.0 | 3.2 |
| 1143 | 22.8 | 11.8 | 9.9 | 7.7 | 2.5 | 2.5 |
| 957 | 13.7 | 8.9 | 7.8 | 5.8 | 1.7 | 2.0 |
| 500 | 10.8 | 7.4 | 3.9 | 0.8 | 1.1 | 0.9 |
| Ground state | 14.6 | 6.9 | 4.7 | 3.2 | 2.1 | 2.2 |

If relaxation really proceeds in steps, how large are the steps? The fact that the $v_9=1$ state relaxes significantly more slowly than the higher energy states implies that at low energies 500 $\mathrm{cm}^{-1}$ is somewhat difficult to shed in one step. It may be that the relaxation of the $v_9=1$ state is via the relaxation of the $v_{12}=1$ state at 404 $\mathrm{cm}^{-1}$, but the conclusion is unchanged. One of these two states is serving as the bottleneck in the relaxation process.

If the energy lost/collision were too small, the observed relatively fast increase of the ground-state population could not occur. As an example, consider the case of collisions of $SF_6$ with vinoxy shown in Fig. 5. One can roughly estimate the average energy loss/collision using the data on $SF_6$. The half time for relaxation is ~20 μs at a number density of $10^{16}$. The vibrational relaxation rate constant varies with energy, but we adopt a mean value of $20\times10^{-12}\,\mathrm{cm}^3\,\mathrm{mol}^{-1}\,\mathrm{s}^{-1}$. In about 20 μs a typical radical loses about 1000 $\mathrm{cm}^{-1}$ of energy. The number of relaxing collisions in this time is therefore ~4. The average energy loss/collision is then 250 $\mathrm{cm}^{-1}$. We conclude that in a typical collision 200–300 $\mathrm{cm}^{-1}$ of energy are lost. The donor radical changes its vibrational state to one of an abundant set of lower ones and the energy released appears mainly as relative translation and rotation. The vibrations of the acceptor molecules seem to play little role. For example, $O_2$, which has a vibration frequency of 1560 $\mathrm{cm}^{-1}$, was not an effective relaxer for the frequency $\nu_4$, which is 1543 $\mathrm{cm}^{-1}$. Even the presence of a soft torsional mode as in ethane seems to make little difference. Ethane is more effective than methane but only in the ratio of their molecular sizes. The torsional mode in the hot molecule makes a large difference in relaxation, as was shown by Parmenter.[16] Molecules with a soft torsional mode relax an order of magnitude faster than rigid molecules.

## D. Vibrational distribution of the vinoxy reaction product

Figures 6 and 7 show the LIF excitation spectrum of reaction produced vinoxy from four different alkenes. All four spectra end at around 3000 $\mathrm{cm}^{-1}$, indicating that no vinoxy has more vibrational energy than that. The hot bands which have been identified are labeled. Most of the other bands, especially those clustered to the red of the strong $0_0^0$ and $4_1^0$ bands, are sequence bands. For lack of signal and resolution some of the higher energy bands can not be assigned. However, almost all of the bands with intensity ⩾3% of the strongest $4_1^0$ band have been detected in this work. The relative populations of the various vibrational states of vinoxy given in columns 4–7 of Table I were obtained by dividing the peak intensity of each assigned band by the F–C factor for that band found in column 3. The sum of the populations was normalized to 1. The average energies listed in Table III were obtained by summing the products of the populations in columns 4–7 and the energies in column 2.

Ethylene can produce vinoxy by a direct reaction. The other three alkenes can produce vinoxy by two mechanisms.

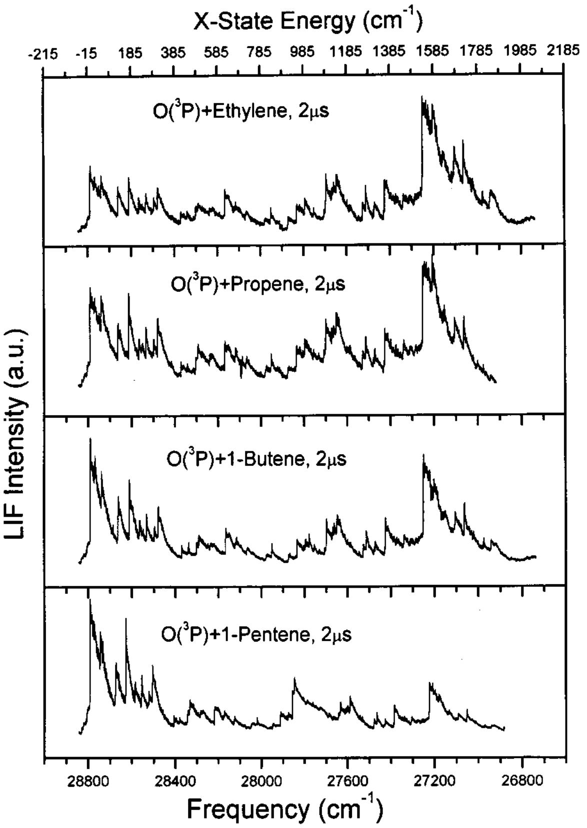

FIG. 6. LIF excitation spectra of the vinoxy product of the reaction of O($^3P$) with ethylene, propene, 1-butene, and 1-pentene in the energy ranges 0 to 1600 cm$^{-1}$.

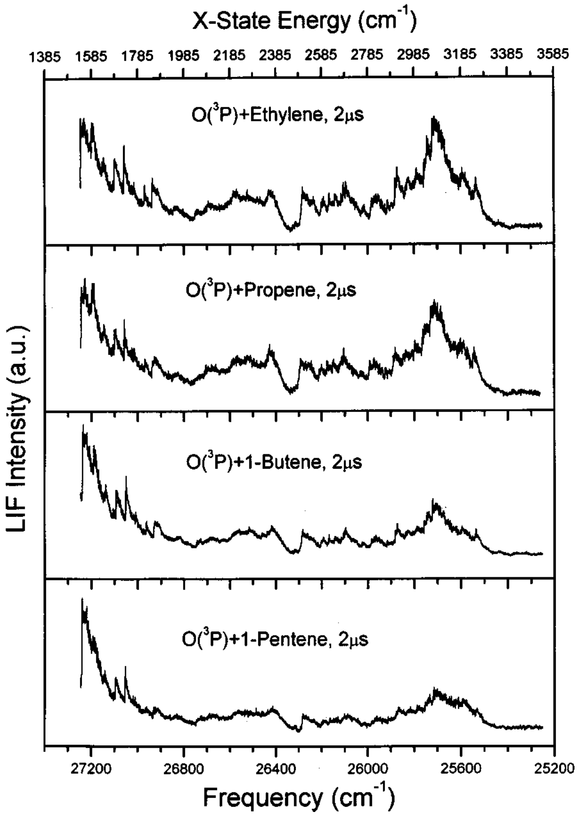

FIG. 7. Same as Fig. 6 for redshifts 1500 to 3000 cm$^{-1}$.

The O atom can attack the substituted carbon atom, in which case the radical leaves at once on the triplet surface, or the O atom can attack the unsubstituted carbon atom. Because of hyperconjugation the more negative carbon atom is the unsubstituted one and therefore the more likely target of the electrophilic O atom. In these reactions H atoms are not formed in appreciable amounts.[11] That means that a 1–2 H atom migration occurs and only then is a radical released

$$\begin{aligned} \mathrm{RCH{=}CH_2+O(^2\mathit{P})} &\rightarrow [\mathrm{RCH{-}CH_2O}] \\ &\rightarrow [\mathrm{RCH_2{-}CH{=}O}] \\ &\rightarrow \mathrm{R\cdot + \cdot CH_2{-}CH{=}O}. \end{aligned} \tag{5}$$

The exoergicity of this reaction is 5940±800, 9400 ±800, 9850±800, and 10 000±800 cm$^{-1}$ for ethylene, propene, butene, and pentene, respectively. An aldehyde is formed transiently. The behavior of this hot aldehyde depends on its length. In every case the weakest bond breaks. With acetaldehyde at these energies the channel of decomposition is to $CH_3$+CHO. Propanal releases a little CHO, and butanal and pentanal none. Instead, the alkyl and vinoxy radical pair is released. There may well be other product channels, but the present paper is devoted solely to the channels producing vinoxy.

A remarkable intramolecular vibrational redistribution (IVR) is shown in Figs. 6 and 7. The average vibrational energy in the vinoxy products of the reactions of O($^3P$) with ethylene, propene, 1-butene, and 1-pentene is 2100, 1800, 1570, and 1180 cm$^{-1}$, respectively. The longer the alkyl chain the cooler the vibrational distribution. This is particularly obvious when looking at the strong peaks due to $4^0_0$, $4^0_1$, and $4^0_2$. The implication is that the reaction complex lives long enough to permit the vibrational energy to be distributed in both the vinoxy and the alkyl radical. The time scale for IVR is only tens of ps, which may be shorter than the time for intersystem crossing to the ground singlet state. A hot alkanal is formed and then, as it breaks up, it releases energy democratically into vibrational modes of both fragments and into rotation and translation. While the system is probed two μs after generation of the oxygen atoms, the average age of the vinoxy radicals is then only one μs. This is sufficient time at the 300 millitorr pressure used for a partial relaxation of the vibrational distribution particularly at the higher energies. However, the qualitative trend going from ethylene to 1-pentene shown in Figs. 6 and 7 results primarily from intramolecular IVR and not from collisions. In one experiment instead of 200 millitorr of propene and

TABLE III. Energy release in the O+alkene→vinoxy+R reaction. All energies are in cm$^{-1}$. Column four is estimated as discussed in the text. $f_V$ is the fraction of the available energy released as vibration. $\langle E_V(\mathrm{R})\rangle$ is calculated from Eq. (6).

| Alkene | $E_{\mathrm{AVL}}$ | $\langle E_V(\mathrm{vinoxy})\rangle$ | $\langle E_V(\mathrm{R})\rangle$ | $\langle f_V\rangle$ | $\langle f_{T+R}\rangle$ |
|---|---|---|---|---|---|
| Ethene | 5 940 | 2100 | 0 | 0.35 | 0.65 |
| Propene | 9 400 | 1800 | (600) | 0.26 | 0.74 |
| 1-butene | 9 550 | 1570 | (1740) | 0.34 | 0.66 |
| 1-pentene | 10 000 | 1180 | (2230) | 0.34 | 0.66 |

100 millitorr of $SO_2$, 200 millitorr of $SO_2$ and 100 millitorr of propene were used with no apparent change in the spectrum.

The average H atom translational energy for the $O(^3P)+C_2H_4 \rightarrow H+CH_2CHO$ reaction was measured by Loison *et al.* using a beam and by Quandt *et al.* in a gas cell.[11,13] The results were concordant with the average kinetic energy $3990 \pm 300\,cm^{-1}$. The energy release from this reaction, not including the relative translational energy of the photoproduced $O(^3P)$ atom, is $5940 \pm 800\,cm^{-1}$. (The uncertainty is almost entirely due to the uncertainty in the heat of formation of vinoxy.) Thus, the major part of the energy is released as translational energy. Two radicals, in this case the H atom and vinoxy, will repel each other when approaching on a triplet surface and, conversely, when separating on a triplet surface considerable kinetic energy is generated. Incidentally, examination of the state distributions of Table I shows that the populations of states with one or two quanta in the mode $\nu_4$, that is $4_1$ and $4_2$, are quite small even though the transitions $4_1^0$ and $4_2^0$ are the strongest in the LIF spectrum. Their very large F–C factors are the cause of the high intensities and not a large population.

While only the average vibrational energy of vinoxy is known, one can estimate the vibrational energy of the other product, R, by making a simple assumption. Suppose that all C–H stretches are considered to be spectators, in that they are not involved in the reaction or in the subsequent IVR. Next, assume that the average energy/mode in the leaving radical is the same as that in vinoxy. Thus, the unknown vibrational energy of the radical R is given by the equation:

$$\langle E_V(\mathrm{R})\rangle = (n/9)\langle E_V(\mathrm{vinoxy})\rangle, \tag{6}$$

where $n$ is the number of vibrational modes in R minus the C–H stretches. The results, shown in Table I, indicate that about a third of all the available energy is released as vibrational energy; therefore, conversely about two-thirds of the available energy is released as translation and rotation. This sort of partition is associated with separation on a repulsive surface, often a triplet surface. It might be argued that a barrier would result from the fact that the vinoxy has different structures when it is free and when it is part of an aldehyde. However, Harding and Klippenstein have recently shown that there is no barrier to combination of a hydrogen atom with an allyl or propargyl radical.[17] The general conclusion is that even if one radical has to undergo extensive structural changes there is no barrier to combination on the singlet surface.

There are two pieces of evidence that the vinoxy from the ethylene reaction is produced on the triplet surface. One is the large release of translational energy. The other is a study using crossed beams by Schmoltner *et al.*, which showed that the product angular distribution of the $CH_3+HCO$ channel was forward–backward symmetric, whereas the $H+CH_2CHO$ chanel was not forward–backward symmetric.[18] The interpretation, supported by theory, was that the vinoxy was formed directly on the initial triplet surface on a time scale of a molecular rotation. An opposing view is held by Abou-Zied and McDonald.[19] They photodissociated a van der Waals complex of $NO_2$ and ethylene and measured the rise time of the vinoxy LIF, which was $217 \pm 38$ ps, and they deny the anisotropy claimed by Schmoltner *et al.* It is still possible that the intersystem crossing rate is slower than the dissociation rate of the reaction complex, so that products separate on the triplet surface. Another possibility is that the mechanism in the van der Waals complex is different from that with the free oxygen atom. The large translational energy release in the reactions of the higher alkenes inferred from their small vibrational energy implies separation on a triplet surface. This is contrary to previous views.[11,17,20] Molecular beam and ps experiments on olefins other than ethylene are needed to resolve this problem.

## IV. SUMMARY

The redshifted LIF excitation spectra of nascent vinoxy radicals show that they are excited in many different modes with different numbers of quanta. Moreover, the vinoxy reaction product is cooler the larger the reaction complex, thus showing that internal vibrational redistribution takes place prior to formation of the products. The vinoxy photoproduct at 193 nm of an alkyl vinyl ether has a maximum of 5600 $cm^{-1}$ of internal energy.

The many methods of measuring vibrational relaxation have been reviewed by Flynn, Parmenter, and Wodtke.[21] This paper has demonstrated a new method using LIF spectroscopy. An ideal experiment would involve the preparation of the desired molecule, by photochemical means if necessary, and measuring the LIF signal as a function of time and energy. The quantitative description is as follows. Let $f(E,t)$ be the fraction of molecules with internal energy $E$ at the time $t$. $f(E,t)$ increases because of relaxation from higher energy states and decreases by relaxation to lower energy states. The time dependence of the number densities is given by a master equation

$$df(E,t)/dt = -\int_0^\infty \{k(E,E') - k(E',E)\} n_R f(E',t)\,dE'. \tag{7}$$

$k(E,E')$ is the rate constant for a collision-induced transition from an internal energy $E$ to a usually smaller energy $E'$ and $n_R$ is the number density of relaxing buffer gas molecules. The initial distribution $f(E,0)$ is obtained by dividing the LIF excitation spectrum by the emission spectrum following excitation at the band origin as in Fig. 1 and then normalizing the area under the distribution curve to unity. It has the following advantages. It measures relaxation processes in the chemically significant ground state rather than in an excited electronic state. The time dependence of the population at a given energy can be measured, providing a powerful overall view of the relaxation. At low energies a definite energy means a particular vibrational state. At high energies where resolution is no longer possible it probes the time dependence of a set of near-degenerate states. In this sense it is related to the transient hot UV spectral methods of Troe.[22] Its principal drawback is that Franck–Condon factors limit the range of energies it can probe. For example, Brock and Rohlfing showed that the vibrationless $B$ state of vinoxy radiates only over a range of 7500 $cm^{-1}$. A minor limitation is that the energized molecule must exhibit fluorescence. The method is not limited to radicals, however. Stable molecules such as benzene, toluene, and acetylene are much more convenient examples.

## ACKNOWLEDGMENTS

This research was supported by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy, Sciences, Office of Science, U.S. Department of Energy. Special thanks are due to Eric Rohlfing, who supplied the data in the third column of Table I enabling calculation of vibrational state populations.

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