Laser-induced fluorescence spectroscopy of the ketenyl radical

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We report the first laser-induced fluorescence (LIF) excitation spectrum of the ketenyl radical, HCCO, which is produced by the 193 nm photolysis of ketene in a free jet expansion. A series of vibronic bands in the $\tilde{B}\ ^2\Pi - \tilde{X}\ ^2A''$ system are observed. The LIF band positions and rotational structures are in excellent agreement with those of a recent photofragment yield (PFY) spectrum [D. L. Osborn *et al.*, J. Chem. Phys. (to be published)] from the origin at 33 424 cm^{-1} to 35 100 cm^{-1} . At higher energies the LIF spectrum breaks off sharply due to a rapid increase in the rate of predissociation. The lifetime of the vibrationless level of the $\tilde{B}$ state is less than 1 ns; the estimated quantum yield of fluorescence is $\sim 10^{-3}$. *© 1997 American Institute of Physics.* [S0021-9606(97)02526-9]

The ketenyl radical, HCCO, is a critical intermediate in a variety of combustion reactions, including the dominant pathway for the oxidation of acetylene, $C_2H_2 + O(^3P) \rightarrow HCCO + H$.[1–3] Because of its importance in combustion, there is a strong incentive for discovering an optical means of detecting HCCO in combustion environments and in chemical kinetics studies. Ketenyl radical has been spectroscopically characterized in the submillimeter[4,5] and infrared regions[6,7] and the infrared (IR) absorption at 2023 cm^{-1} has been used in kinetic studies of HCCO.[8] While submillimeter and IR spectra provide detailed information on the low-lying rovibrational levels of the ground-state of ketenyl, useful spectroscopic diagnostics [such as laser-induced fluorescence (LIF)] are typically based on electronic transitions. Until recently, the observation of an electronic band system that can be conclusively assigned to the ketenyl radical has remained elusive. Inoue and Suzuki[9] found an ultraviolet (UV) band system with LIF following the reaction the reaction of $O(^3P) + C_2H_2$ that they assigned to HCCO. However, this spectrum was later shown to be due entirely to the $\tilde{A}\ ^1A_2 - \tilde{X}\ ^1A_1$ system of H_2CO.[10] Krishnamachari and Venkatasubramanian reported a series of absorption bands in the 308–367 nm region for a transient obtained in the flash photolysis of oxazole and isoxazole, which they assigned to HCCO.[11] This observation has never been duplicated.

Recently, Neumark and co-workers[12,13] positively identified an extensive electronic band system of ketenyl in the 208–300 nm region using fast radical beam photofragment translational spectroscopy. In these experiments, a mass-selected beam of $HCCO^-$ is photodetached to form a fast beam of neutral HCCO and the photodissociation of the neutral radical is induced in another excitation step. Monitoring the total fragment production as a function of excitation wavelength gives a photofragment yield (PFY) spectrum. In addition, Osborn *et al.*[12] measured the translational energy and angular distributions of photofragments at several excitation energies for the $CH(\tilde{a}\ ^4\Sigma^-) + CO$ and $CH(\tilde{X}\ ^2\Pi) + CO$ channels. The low energy portions of the PFY spectrum showed rotational structure and a pair of bands near 33 424 cm^{-1} were assigned as the $F_1 - F_1$ and $F_2 - F_2$ components of the origin of the $\tilde{B}\ ^2\Pi\ (K'=1) - \tilde{X}\ ^2A''\ (K''=1)$ parallel transition.[12] This observation and assignment is consistent with recent *ab initio* calculations[14] on HCCO which predict that the bent ground state and the linear first excited state, $\tilde{A}\ ^2\Pi(^2A')$, form a Renner–Teller pair. The second excited state, $\tilde{B}\ ^2\Pi$, is found to be linear but also exhibits Renner–Teller vibronic coupling, induced primarily by the *trans* bend vibration. The ground state has a normally small spin-rotation splitting,[4] but in the $\tilde{B}$ state the spin of the unpaired electron is strongly coupled to the unquenched orbital angular momentum. Thus there is a large spin–orbit splitting between the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ levels of the vibrationless level of the $\tilde{B}$ state, which manifests itself as the $F_1 - F_1$ $(J = N + 1/2)$ and $F_2 - F_2$ $(J = N - 1/2)$ subbands separated by 41 cm^{-1}. At 0.08 cm^{-1} resolution the PFY origin spectrum showed no evidence of homogeneous broadening due to predissociation. This places a lower limit on the lifetime of the vibrationless level of the $\tilde{B}$ state of $\tau \geqslant 150$ ps. (This limit is based on a more conservative criterion for the onset observable broadening than that used in Ref. 12, where a limit of $\tau \geqslant 300$ ps was quoted.) Based on this observation, Osborn *et al.* speculated that the fluorescence quantum yield may be large enough to observe the $\tilde{B} - \tilde{X}$ spectrum of HCCO by laser-induced fluorescence.

In this letter we describe the first detection of HCCO via LIF, using exactly the $\tilde{B} - \tilde{X}$ band system observed in PFY by Osborn *et al.* We produce jet-cooled HCCO by the photolysis of ketene, CH_2CO, at 193 nm in the early portion of a free jet expansion. The 193 nm photolysis of ketene has been used as a source of HCCO in gas-phase IR studies[6,7] and the photolysis yield for H+HCCO has recently been determined to be ~37%.[15] The ketene is seeded at 10% concentration in helium buffer gas and the mixture is expanded through a 1 mm diam orifice by a piezoelectrically actuated pulsed valve. Photolysis occurs in the first 1–2 mm of the expansion and

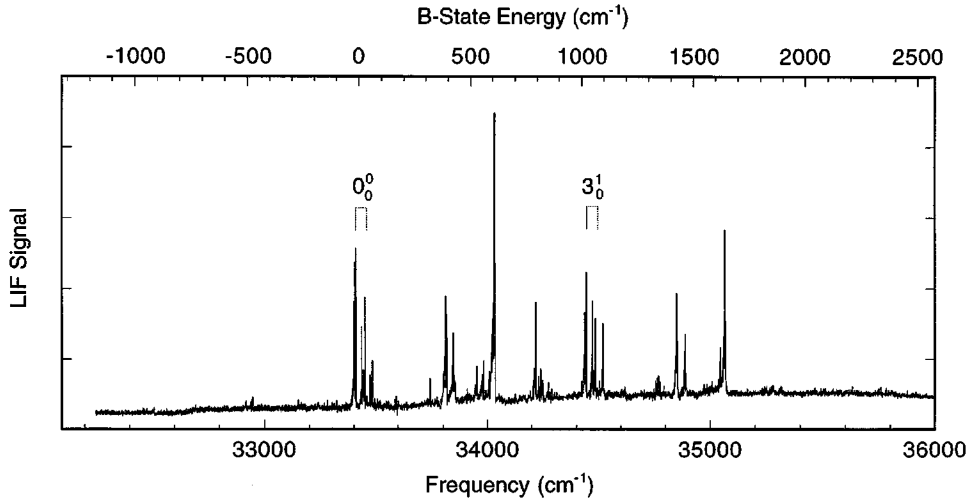

FIG. 1. A LIF survey spectrum of the $\tilde{B}\ ^2\Pi-\tilde{X}\ ^2A''$ band system of jet-cooled HCCO. This spectrum is a concatenation of several separate spectra and the signal has not been normalized.

the LIF excitation laser intersects the jet 15 mm downstream of the nozzle. The remainder of the apparatus is identical to that used in our recent studies of the formyl[16] and vinoxy[17] radicals. The HCCO fluorescence is detected with a photomultiplier tube (PMT) through a combination of a long-wave-pass filter (>320 nm) and an interference filter, which is centered at 400 nm and has a bandpass of 50 nm. The PMT signal is amplified and then integrated with a boxcar averager. The LIF excitation laser is a frequently-doubled, Nd:YAG-pumped dye laser with a bandwidth of ~ 0.16 cm^{-1} in the UV and a pulse duration of 5–6 ns.

Figure 1 displays a survey of the LIF spectrum of the $\tilde{B}\ ^2\Pi-\tilde{X}\ ^2A''$ system of jet-cooled HCCO. This spectrum is a concatenation of several spectra and has not been normalized by the energy in either the photolysis or excitation laser pulses. However, both the photolysis conditions and the excitation pulse energy were kept fairly constant during these scans. Because the absorption cross section of ketene at 193 nm is very small ($\sim 10^{-19}$ cm^2),[18] the HCCO LIF signal is optimized at fairly high photolysis energies (5–10 mJ/pulse in a 2–3 mm diam spot). At these intensities we observe LIF due to the UV band system(s) of C_3 ,[19,20] which is probably produced by multiphoton dissociation and recombination. The fluorescence from C_3 is clearly differentiated from that of HCCO because the former is very long lived ($0.3\ \mu s < \tau < 2.5\ \mu s$) (Refs. 19,20) while the latter is very short lived ($\tau \lesssim 1$ ns; see below). We monitor the C_3 background with a separate boxcar averager whose gate is set to detect only long-lived fluorescence. In a few regions of the survey spectrum in Fig. 1 this C_3 background, which never exceeds 10% of the HCCO signal, has been subtracted from the HCCO signal. The HCCO LIF signal scaled linearly with excitation pulse energy up to the highest energy used in these experiments, 0.4 mJ/pulse in a spot size that is ~ 2 mm in diameter.

As labeled in Fig. 1, the first strong feature in the LIF spectrum is the band assigned as 0_0^0 in the PFY spectrum. Figure 2 shows a detailed view of the rotational structure of the $K'=1-K''=1$, F_1-F_1 component. The agreement between the rotational structure we observe in LIF and that seen by Osborn *et al.* with PFY is excellent and confirms that the carrier of the LIF spectrum is indeed HCCO. As noted above, the ground state is best described by a small spin-rotation splitting, corresponding to Hund's case (b) coupling in a linear molecule. By contrast, the upper state is more accurately described by Hund's case (a) coupling, and so we label the rotational branches in Fig. 2 in that notation. [Osborn *et al.* use case (b) labeling.[12]]

We observe a weak band at 32 930 cm^{-1} that lies to the red of the band assigned as 0_0^0 in the PFY spectrum. However, by varying the photolysis and expansion conditions, we find that the intensity in this band can be altered dramatically relative to the intensity of the assigned origin band. Thus, we conclude that it must be a vibrationally hot band and that the 0_0^0 assignment made in the PFY spectrum is correct. If the upper level of the hot band is the vibrationless level of the $\tilde{B}$ state, then the corresponding ground-state energy of 494

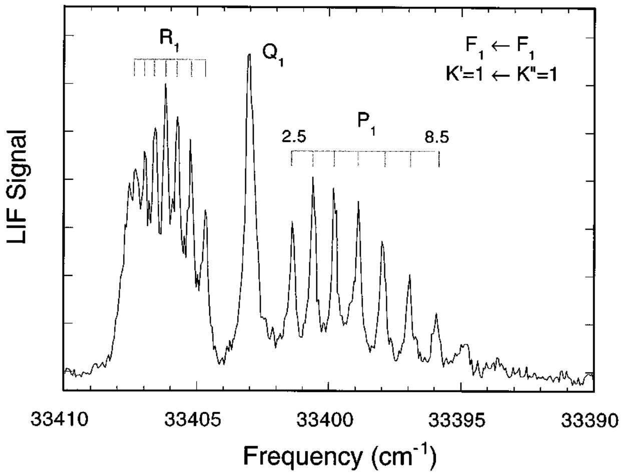

FIG. 2. Rotational structure of the F_1-F_1 component of the $\tilde{B}\ ^2\Pi(K'=1)-\tilde{X}\ ^2A''(K''=1)$ origin band. Rotational labels are appropriate to Hund's case (a) coupling.

cm^{-1} is best assigned to the CCH bend, ν_6'', which is calculated at 450–528 cm^{-1} at various levels of theory[14] and at 484 cm^{-1} at the QCI level.[21]

We have measured the fluorescence decay for the 0_0^0 band and find that it is virtually indistinguishable from the excitation function (true excitation pulse plus temporal response of the detection/amplification electronics). From a fit to this decay using a convolution of the excitation function and an exponential decay, identical to that performed for the rapid decays of the vinoxy radical,[17] we can firmly establish that the origin lifetime must be less than 1 ns. With the lower limit set by the lack of broadening in the PFY spectrum noted above, we can then bracket the lifetime of the vibrationless level of the $\tilde{B}$ state as 150 ps$\leqslant\tau\leqslant$1 ns.

In order to estimate the fluorescence quantum yield, we calculate the radiative lifetime of the $\tilde{B}$ state from a singles-only CI calculation of the $\tilde{B}-\tilde{X}$ oscillator strength, $f\sim 0.03$.[22] For calibration, we compare the oscillator strength calculated using the same method for the $\tilde{B}\ ^2A''-\tilde{X}\ ^2A''$ transition of vinoxy radical, for which the radiative lifetime is known.[17] In that case, we find that the calculated oscillator strength is 7 times too large, i.e., it predicts a lifetime that is 7 times shorter than the observed lifetime of the $\tilde{B}-\tilde{X}$ origin, which is virtually free of predissociation.[17] Reducing the calculated oscillator strength for HCCO by a factor of 7 gives $f\sim 0.004$, which yields a radiative lifetime of ~600 ns. While this approach is quite crude (there is no accounting for the spectral distribution of the emission, for example), it provides an order-of-magnitude estimate of the fluorescence quantum yield, which is 10^{-3}. This small quantum yield is consistent with the signal to noise of our LIF spectra and may not bode well for the use of the $\tilde{B}-\tilde{X}$ system as an optical diagnostic of HCCO. However, in atmospheric pressure flames fluorescence quenching is so rapid that the collisional lifetime of an electronically excited state may be on the order of a nanosecond.[23] Thus, if the loss of fluorescence due to quenching is comparable to the loss due to predissociation then the $\tilde{B}-\tilde{X}$ system may still prove useful as a LIF diagnostic of HCCO in some flames. Finally, preliminary PFY spectra of DCCO (Ref. 24) do not show dissociation in the low-energy region near the HCCO origin, suggesting that the fluorescence quantum yield of DCCO is much larger. We are currently pursuing the LIF spectroscopy of DCCO, produced by photolysis of CD_2CO.

The agreement in band positions between the LIF spectrum and the PFY spectrum in the region from 33 400 cm^{-1} to 35 100 cm^{-1} is very good. However, the relative intensities are quite different in the two spectra, which is not surprising since LIF probes levels that fluoresce well while PFY sees only levels that predissociate. For example, the bands at 33 742 cm^{-1} and 34 723 cm^{-1} are strong in the PFY spectrum but are quite weak in the LIF spectrum. Even more dramatic is the sharp cutoff in the LIF spectrum above 35 100 cm^{-1} ($\geqslant$1700 cm^{-1} in the $\tilde{B}$ state) where the PFY spectrum exhibits an increasingly large number of very strong bands. Osborn *et al.* observe homogeneous broadening in the band at 35 333 cm^{-1} (1900 cm^{-1} in the $\tilde{B}$ state) that implies an excited-state lifetime of ~40 ps. Compared to our bracket of the origin lifetime, this corresponds to a 4–25-fold decrease in fluorescence quantum yield relative to the origin. The dramatic loss of LIF intensity that we observe seems more consistent with the larger decrease in quantum yield, i.e., with the upper limit ($\tau\leqslant$1 ns) for the origin lifetime. The sudden increase in the predissociation rate at 35 100 cm^{-1} is indicative of a pronounced change in the nature of the predissociation dynamics. Interestingly, this rate increase occurs at exactly the energy at which the translational energy distributions show a change in the dominant dissociation channel from spin-forbidden, CH($\tilde{a}\ ^4\Sigma^-$)+CO, to spin-allowed, CH($\tilde{X}\ ^2\Pi$)+CO.[12] Thus, intersystem crossing from the $\tilde{B}\ ^2\Pi$ state of HCCO to the $\tilde{a}\ ^4A''$ state, which correlates with CH($\tilde{a}\ ^4\Sigma^-$)+CO, dominates the predissociation for the first 1700 cm^{-1}. At higher energies, more rapid internal conversion to the ground state, which correlates with CH($\tilde{X}\ ^2\Pi$)+CO, becomes the primary pathway for predissociation.

The vibronic structure of the PFY spectrum is dominated by a progression assigned to the symmetric combination of the C–C and C–O bond stretches, ν_3'.[12] We observe only the first member of this progression in the LIF spectrum, the 3_0^1 band at 34 461 cm^{-1}. The rotational structure of this band is very similar to that of the 0_0^0 band, and should be readily analyzed. The observed value of the fundamental frequency of ν_3', 1037 cm^{-1}, is in good agreement with the (unscaled) *ab initio* value of 1097 cm^{-1} (EOM-IP with PVTZ basis from Ref. 14). All of the bands in the LIF spectrum to the blue of the 3_0^1 band are simply combinations of the bands observed at lower energies with the 3_0^1 band. Since the other two stretching vibrations are higher in frequency than ν_3', the bands between 0_0^0 and 3_0^1 can only involve the *cis* and *trans* bending vibrations of π symmetry. The *trans* bend is calculated to be strongly Renner–Teller active ($\omega_5=328$ cm^{-1} and $\varepsilon=-0.573$), while the *cis* bend exhibits a much smaller Renner parameter ($\omega_4=525$ cm^{-1} and $\varepsilon=-0.017$).[14] Both odd and even bending levels should be observable; the former will possess states with an overall vibronic symmetry of Σ, i.e., $K'=0$ states. The rotational structure of bands terminating on these Renner–Teller levels is somewhat complicated, but the effective Hamiltonian is well known[25–27] and detailed rotational analyses should be possible. In future experiments, we shall obtain fully rotationally resolved LIF spectra of HCCO (and DCCO) using a high-resolution (0.03 cm^{-1}) UV excitation source based on a single-mode optical parametric oscillator/amplifier. Such spectra will also provide better measurements of homogeneous line broadening that can serve to more accurately determine excited-state lifetimes.

The initial LIF spectra of HCCO reported here form the basis for many more spectroscopic studies of this key combustion radical. In addition to the high-resolution LIF experiments on HCCO and DCCO mentioned above, we shall pursue other techniques to obtain excitation spectra of the more rapidly predissociating levels in the $\tilde{B}$ state. These may include a two-color resonant four-wave mixing (TC-RFWM) scheme analogous to spectral hole-burning that we have recently used on vinoxy radical[17] and resonant enhanced multiphoton ionization (REMPI). The TC-RFWM technique has the advantage of being a double resonance approach that is purely absorption based. Conversely, REMPI has far greater sensitivity than TC-RFWM, but the ionization rate out of the electronically excited state must be made comparable to the rate of predissociation. We also hope to characterize the $\tilde{X}\ ^2A''$ and $\tilde{A}\ ^2\Pi(^2A')$ states through dispersed fluorescence (DF) and/or stimulated emission pumping (SEP) spectroscopy utilizing the $\tilde{B}\ ^2\Pi$ state as an intermediate. The success of DF or SEP utilizing fluorescence depletion will depend critically on the fluorescence quantum yield. However, TC-RFWM schemes for SEP (Refs. 28,29) may be applicable in cases where the electronically excited state is heavily predissociated. In summary, the recent PFY spectrum and these initial LIF spectra of HCCO opened the door for a whole gamut of spectroscopic studies of the ketenyl radical.

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