



Electronic spectroscopy of the $\tilde{B}(0, 0, 0) \leftarrow \tilde{X}(0, 0, 0)$ transition of DCO and lifetimes and relative quantum yields of the $\tilde{B}(0, 0, 0)$ state

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ABSTRACT

We have measured the laser induced fluorescence excitation spectrum of the origin of the DCO $\tilde{B}(^2A') \leftarrow \tilde{X}(^2A')$ transition under a variety of experimental conditions, ranging from cooled to 7 K in a supersonic jet, to nascent in the photolysis of D₂CO. By analysing successively more complex spectra we have derived rotational, centrifugal distortion, and spin-rotation coupling constants that provided the best fit to the experimental frequencies. Fluorescence lifetimes were measured for 35 rotationally-resolved excited states, which provided relative quantum yields for these states. Unlike HCO, the lifetimes showed only a weak dependence on *N* and *K_a*, evincing a weaker coupling between the \tilde{A} and \tilde{B} states in DCO than HCO. Intensity ratios for pairs of transitions with the same lower state were used to extract the transition moment angle, $\theta = 44.6 \pm 2.5^\circ$ and the axis switching angle, $\phi = 3.1 \pm 0.5^\circ$ for the $\tilde{B}-\tilde{X}$ transition. Both angles are consistent with the expected change upon deuteration of HCO.

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1. Introduction

The formyl radical, HCO, is an important constituent in hydrocarbon combustion [1], as well as the “low temperature” combustion environment of the Earth’s atmosphere [2], and the very low temperature of the interstellar medium. It is formed predominantly from H-abstraction or decomposition (thermal or photolytic) from aldehydes, or H-atom attachment to CO, and plays an important role in the overall H-atom balance in these environments.

There have been numerous investigations of the spectroscopy of HCO, including microwave, fluorescence emission, laser induced fluorescence (LIF), stimulated emission pumping (SEP), and resonance-enhanced multiphoton ionisation (REMPI) [3–12]. These studies have led to quite a thorough understanding of the electronic and nuclear structure of HCO in the \tilde{X} , \tilde{A} , and \tilde{B} states, which, in turn, has enabled the optical spectrum of HCO to be used as a probe of the role of HCO in chemical processes.

The most detailed work on the $\tilde{B}-\tilde{X}$ transition of HCO was performed by Chen and co-workers in a series of papers which provided considerable detail, including measurement of state-specific quantum yields, analysis of the spin-rotation coupling, determination of the axis switching angle and axis-switching line strengths, and Coriolis coupling [6–9]. As a consequence of this

detailed spectroscopic analysis, the LIF spectrum of the $\tilde{B}-\tilde{X}$ transition has been used as a spectroscopic probe of reaction dynamics involving HCO as a reaction product from a wide variety of reactants, including formaldehyde [13–16], acetaldehyde [17–20], propanal [21,22], propenal [23] and glyoxal [24].

Isotopic labelling is one of the most powerful chemical techniques for investigating molecular structure, mechanisms and reactivity, and finds applications from pure spectroscopy to medical imaging and astrophysical models. Indeed our motivation for the present work arises from our recent experiments on isotopically-labelled acetaldehyde [25] and formaldehyde [26] where we have been exploring the photodissociation dynamics, in particular the chemical mechanism that produces the DCO product. We have measured high resolution LIF spectra of the $\tilde{B}-\tilde{X}$ transition in the DCO fragment under a variety of conditions. However, the quality of the published spectroscopic data concerning this transition is more incomplete than for HCO and we were unable to infer product state distributions from the spectrum. For this reason, we have carried out a detailed spectroscopic investigation of the $\tilde{B} \leftarrow \tilde{X}$ transition of DCO, using the previous HCO work of Chen to guide our way.

The $\tilde{B} \leftarrow \tilde{X}$ spectrum of jet-cooled DCO has been studied previously using both REMPI [4] and LIF [27]. This has resulted in a good set of measurements of the vibrational structure of the \tilde{B} state, including measurements of all three vibrational frequencies and six anharmonicity constants. Cool and Song also made a preliminary examination of the rotational profiles in the $\tilde{B} \leftarrow \tilde{X}$ transitions, though with insufficient resolution to adequately distinguish individual lines [4]. A more thoroughly resolved analysis was made by

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Gripp and co-workers, including the simulation of DCO spectra with a rotational temperature of 10 K for a number of vibrational bands [27].

The $\tilde{X}(0, 0, 0)$ state has been studied by millimetre- and submillimetre-wave techniques [28,29] yielding a fairly complete set of rotational constants, including spin-rotation and centrifugal parameters. Tobiason et al. [30] measured the dispersed fluorescence spectrum of DCO, yielding a large number of vibrational energies and Franck–Condon factors. A summary of \tilde{X} and \tilde{B} state parameters of DCO and HCO relevant to this work is collected in Table 1.

To have enough insight into the DCO spectrum to allow the extraction of dynamical information requires the fulfilment of two goals. Firstly we must extend our understanding of the DCO rotational structure of the $\tilde{B}(0, 0, 0) \leftarrow \tilde{X}(0, 0, 0)$ transition from the simulation of a 10 K spectrum, in which typically only $J \leq 5$ and $K_a \leq 1$ are observed, to modelling of nascent spectra with population of much higher rotational states. Secondly we must make a full account of the intrinsic line strengths of each transition in order that we may extract relative populations of rotational states. This requires information about the relative transition strengths of the hybrid *a*- and *b*-type rotational band structure, the intensity effects of axis switching and the relative fluorescence quantum yields for the various excited states. While these quantities have been extensively analysed for HCO [6–9], no such information is yet available for DCO.

2. Experimental methods

Deuterated formaldehyde (D_2CO) (Acros, 99% D-atom) was expanded in a free jet of He in a similar manner as reported previously for H_2CO experiments [13]. D_2CO was excited at a range of distances downstream from the nozzle orifice by a Nd:YAG-pumped dye laser with wavelengths corresponding to the $2_0^2 4_0^3$ transition within the $\tilde{A}-\tilde{X}$ band [31]. At these wavelengths, D_2CO is pre-dissociative, forming D + DCO with 200–250 cm^{-1} of energy available to the fragments. DCO was probed via the $\tilde{B}-\tilde{X}$ transition using an excimer-pumped dye laser with an intracavity etalon installed (linewidth = 0.05 cm^{-1}). Nascent DCO spectra were collected with photolysis and probe lasers counter-propagating through the vacuum chamber and intersecting the free jet expansion 15 mm (30 nozzle diameters) below the nozzle orifice.

To simplify the DCO spectra, especially in the early stages of assigning the spectrum, the nozzle was lowered to 9 mm (18 orifice diameters) above the lasers. The pump laser was raised closer to the nozzle and the pump–probe delay time increased up to 1 μs

to allow the DCO to be collisionally-cooled in the expansion, resulting in a colder, thermalised spectrum (~ 10 K).

To investigate variations in the fluorescence lifetime of individual rotational states within the $\tilde{B}(0, 0, 0)$ manifold, 80 of the stronger, well resolved lines of the nascent LIF spectrum were selected. For each peak, the fluorescence decay was collected on an oscilloscope and averaged over 128 laser shots. The averaged trace from the oscilloscope was captured using a custom LABVIEW program.

All spectra, as well as the individual line positions for lifetime measurements, were calibrated using a Coherent Wavemaster wavemeter.

3. Results and discussion

3.1. Line positions and rotational constants

The only well resolved study of the rotational structure of the $\tilde{B} \leftarrow \tilde{X}$ transition of DCO is that of Gripp et al. [27]. In those experiments, jet-cooled DCO was generated by the photolysis of CD_3CDO near the nozzle orifice. The LIF spectrum was then recorded at low resolution for the range 38500–42500 cm^{-1} , while higher resolution spectra were recorded for four vibrational bands, including the electronic origin, with sufficient resolution to separate a number of the spin-rotation doublets. These spectra were simulated with a 10 K Boltzmann population, using the ground state constants of Endo and Hirota [28], which allowed a more accurate determination of the *A*, *B* and *C* constants and spin-rotation coupling parameters for the excited state than was previously possible. The results of the work of Gripp et al. [27] for the electronic origin band are summarised in Table 1.

Three DCO LIF spectra of various rotational temperatures from this work are shown in Fig. 1. Using the parameters of Gripp et al. [27] and Endo and Hirota [28] as a starting point, the coldest of the DCO LIF spectra in panel a was simulated using the computer package PGOPIHER [32]. The inbuilt fitting function of PGOPIHER was used to optimise the \tilde{B} -state rotational constants while keeping the \tilde{X} -state constants fixed. Upon convergence, the process was repeated with successively more complicated spectra in panels b and c. Above panel a are a series of assignments showing the five rotational branches that arise from $K_a'' = 0$ states, which dominate the spectrum at the low temperature. Higher energy branches are becoming more pronounced in the lowest panel where the complex 9R_1 bandhead appears in the bandgap between the 9R_0 and 9P_0 branches. The effect of the coupling between the electron spin and the overall angular momentum of the nuclear framework (spin rotation coupling) is apparent in the doubling of the lines at low *N*

Table 1
Rotational constants for DCO and HCO (all values in cm^{-1}). Uncertainties are reported as 1σ in the last significant figure(s) for this work, and as reported for previous work.

	DCO			HCO	
	$\tilde{X}(0, 0, 0)$	$\tilde{B}(0, 0, 0)$		$\tilde{B}(0, 0, 0)$	
	Endo and Hirota [28]	Gripp et al. [27]	This work	Lee and Chen [7]	Lee et al. [9]
T_0	0	38629.50(3)	38629.533(5)	38695.438	38695.477(7)
<i>A</i>	14.733994(5)	9.172(1)	9.162(3)	15.995(3)	15.976(1)
<i>B</i>	1.281454(9)	1.0927(5)	1.0927(2)	1.1588(5)	1.19351(8) ^a
<i>C</i>	1.171360(9)	0.9743(5)	0.9724(3)	1.0714(5)	1.10763(8) ^a
D_N	$3.4407(11) \times 10^{-6}$		$4.2(12) \times 10^{-6}$		$4.8(1) \times 10^{-6}$
D_{NK}	$-5.8767(9) \times 10^{-5}$		$2.7(8) \times 10^{-5}$		$7.0(6) \times 10^{-5}$
D_K	$1.20356(3) \times 10^{-2}$		$9.15(70) \times 10^{-3}$		
e_{aa}	0.237851(13)	−0.583(5)	−0.641(8)	−1.064(5)	−1.070(4) ^b
e_{bb}	0.000183(57)		−0.011(5)		
e_{cc}	−0.005811(70)		0.005(3)		
$(e_{bb} + e_{cc})/2$		−0.001(3)	−0.008(3)	−0.001(6)	−0.004(6) ^b
$(e_{bb} - e_{cc})/2$			−0.003(3)	−0.002(7)	

^a Calculated from originally reported values as $(B + C)/2$ and $(B - C)/4$, with errors propagated.

^b Calculated from originally reported values as $-(e_{aa} + e_{bb} + e_{cc})/3$ and $-(2e_{aa} - e_{bb} - e_{cc})/6$, with errors propagated.

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