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Nascent vibrational distributions and relaxation rates of diatomic products of the reactions of $O(^1D)$ with CH_4, C_2H_6, CH_3F, CH_2F_2 and CHF_3 studied by time resolved Fourier transform infrared emission

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Abstract

Time resolved Fourier transform infrared (TRFTIR) emission has been used to study the reactions of CH_4, C_2H_6, CH_3F, CH_2F_2 and CHF_3 with $O(^1D)$. One hundred and ninety-three nanomters photolysis of N_2O was used to prepare $O(^1D)$, and emission analysed from $OH(\nu = 1–4)$ for the two hydrocarbons and $HF(\nu = 1–6)$ from CH_3F, CH_2F_2 and CHF_3. For the $O(^1D) + CH_4$ reaction, the nascent OH vibrational distribution showed a population inversion between $\nu = 1$ and 2, and was in excellent agreement with previous laser induced fluorescence and TRFTIR data, as well as with quasi-classical trajectory calculations. Time resolved populations were analysed to yield rate constants for vibrational relaxation of $OH(\nu)$ with CH_4, and found to be consistent with stepwise deexcitation rather than chemical removal being dominant. Reaction with C_2H_6 produced a monotonically decreasing population in $\nu = 1–4$ and more rapid relaxation rates than those with methane. For the fluorinated methanes, nascent vibrational populations in $HF(\nu = 1–6)$ were measured and shown to be very similar, all monotonically decreasing with ν, and fitting the same vibrational surprisal plot, showing a larger than statistical partitioning of the available energy in vibration. Relaxation rate constants of $HF(\nu)$ with the parent fluorinated methane showed values, which increased with increasing H atom content.

Keywords: Laser; Infrared; FTIR; Fluorocarbons; $O(^1D)$

1. Introduction

The gas phase removal processes of electronically excited $O(^1D)$ atoms in potentially reactive collisions with methane CH_4 and fluorinated methanes of the form CH_nF_{4-n} where $n = 1–3$ show several common characteristics. First they are all fast, having rate constants which are close to gas kinetic values for CH_4 and CH_3F of 1.5×10^{-10} and 1.6×10^{-10} cm^3 $molecules^{-1}$ s^{-1}, respectively, and falling with increasing F atom content to a value of 10^{-11} cm^3 $molecule^{-1}$ s^{-1} for CHF_3 [1]. Secondly, they have the possibility of multiple channels in the reaction products as well as contributions from physical quenching to the $O(^3P)$ ground state. For CH_4, the major channel is to form OH [2–4] and quenching is negligible. For the fluorinated species, HF is always found as a major reaction product, and the proportion of collisions leading to quenching increases with F atom content [5–8]. The reactions forming these diatomic products are all highly exothermic, and can form vibrationally excited species. For the process

$$O(^1D) + CH_4 \rightarrow CH_3 + OH(\nu) \quad (1)$$

vibrational levels up to $\nu = 4$ are thermodynamically possible, and levels up to the thermodynamic limit have been observed in previous studies [2,9,10]. For HF formation in conjunction with the appropriate formaldehyde co-product

$$O(^1D) + CH_nF_{4-n} \rightarrow CH_{n-1}F_{3-n}O + HF(\nu) \quad (2)$$

the exothermicities lie in the range 582–642 kJ mol^{-1}, exceeding the HF dissociation energy and thus allowing populations in all vibrational levels of HF. Previous work on the CHF_3 reaction has identified levels up to $\nu = 6$ [6,11] and for the other two fluorinated methanes vibrational excitation up to $\nu = 3$ has been observed [11].

In this paper, we describe TRFTIR measurements of the products of reactions of $O(^1D)$. We observe the nascent vibrational distribution of OH in the reaction of $O(^1D)$ with methane,

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reaction (1), and also with ethane

$$O(^1D) + C_2H_6 \rightarrow C_2H_5 + OH(\nu) \quad (3)$$

and determine the rates of loss of vibrational energy from OH(ν) in collisions with the parent molecule. Vibrational populations of OH in reactions (1) and (3) have been previously measured by laser-induced fluorescence (LIF) [9,10,12] as well by TRFTIR for reaction (1) [2]. Although LIF has higher sensitivity than TRFTIR, the advantage of the latter technique is that all vibrationally excited levels can be observed simultaneously, and this removes the necessity for correction of the observed LIF signals for the different wavelengths of excitation and emission which accompany measurements on a wide variety of vibrational states. For the OH nascent distributions, we compare our results with previous work [2,9,10,12]. Our observations of OH removal rates have been analysed both in terms of a single quantum cascade mechanism and with allowance for reactive removal of OH, with the former providing more consistent comparison with previous data [9,13–16]. We also observe TRFTIR emission from the HF product of reaction (2) for each of the three-fluorinated methanes. We compare our data with previous nascent populations, either measured by the TRFTIR [2] or by laser gain [11,17] and we obtain a complete set of self quenching data which show rate constants which increase monotonically with H atom content of the fluorinated methane.

2. Experimental

The major features of the TRFTIR apparatus have been described previously [18,19] and are summarised here. $O(^1D)$ was produced by the 193 nm photolysis of N_2O in the presence of the reactant and generally an excess of Ar to ensure that rotational (but not vibrational) thermalisation of the OH or HF product was complete on the time scale of the observations. Emission was observed with a Welsh cell arrangement, passed through a FTIR spectrometer operating in the step scan mode (Bruker FS 66/S) and the resultant signal observed normally with 1 μs resolution over a time period typically 200 μs and averaged over 20 laser shots, with signal levels normalised for laser intensity fluctuations. The data consist of time resolved emission as a function of interferometer path difference, and the resultant time resolved interferograms are converted to time resolved emission spectra by fast Fourier transform.

Reagent purities were as follows: N_2O (BOC) > 99.997%, C_2H_6 (BOC) > 99%, CH_4 (BOC) > 99.5%, CH_3F (Lancaster) > 99%, CH_2F_2 (Fluorochem) > 99.7%, CHF_3 (Aldrich) 98%. Total pressures were measured with capacitance manometers (Datametrics Barocell 600 A 10 Torr Head, MKS Batratron 122-AA 1000 Torr head) and converted to partial pressures through measured flow rates through the reaction vessel. All measurements were carried out at room temperature, 295 K.

3. Results and discussion

Our previous TRFTIR emission studies of the 193 nm photolysis of N_2O [19] have shown that infrared emission can be seen from NO (ν) in both the fundamental ($\Delta\nu = -1$) transitions between 1600 and 1900 cm^{-1} for $\nu = 1$–14 and the first overtone ($\Delta\nu = -2$) transitions between 3400 and 3700 cm^{-1} for $\nu = 2$–14 and arising from the reaction of the $O(^1D)$ photofragment with the parent molecule

$$O(^1D) + N_2O \rightarrow 2NO \quad (4)$$

In addition strong emission from the $N_2O(\Delta\nu_3 = -1)$ transitions is seen near 2200 cm^{-1}, the vibrationally excited molecule being formed from energy transfer from the internally excited N_2 cofragment of N_2O photolysis [19]. Hydrocarbon reagents were always added in excess such that reactions (1–3) dominated over (4) for removal of $O(^1D)$ and thus fundamental emissions from OH (observed between 3000 and 3800 cm^{-1}) or HF (2500–4200 cm^{-1}) were not markedly affected by that from NO.

$O(^1D) + CH_4$

The major step in the reaction of $O(^1D)$ with methane is to form the OH radical, accounting for some 70–80% of $O(^1D)$ removal [2–4,20] and the removal rate constant is fast, the recommended value being 1.5×10^{-10} cm^3 $molecule^{-1}$ s^{-1}. Fig. 1 shows a time slice of the fundamental emission region from OH recorded from the $O(^1D) + CH_4$ reaction.

Marked on the figure are the positions of the Q-branches for the ($\Delta\nu = -1$) transitions originating in $\nu = 1$–4, and a simulation is shown which represents the best-fit to a 295 K rotational distribution with the vibrational populations treated as adjustable parameters. Spectral simulations used the *J* dependent transition probabilities calculated by Turnbull and Lowe [21]. The relative populations of vibrational levels 1–4 were extracted at 1 μs intervals and extrapolated to zero time to obtain nascent populations

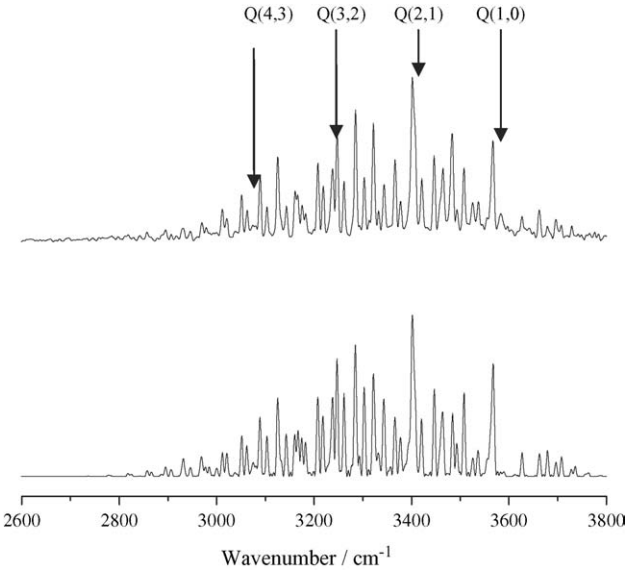

Fig. 1. OH($\Delta\nu = -1$) emission spectrum (upper trace) from $O(^1D) + CH_4$; $p(N_2O) = 200$ m Torr, $p(CH_4) = 500$ m Torr, $t = 10$ μs. Also shown as the lower trace and offset on the vertical scale for clarity is the best-fit OH($\Delta\nu = -1$) simulation for a rotational temperature of 295 K with vibrational populations for $\nu = 1$–4 as the adjustable parameters. The Q-branches of OH($\nu = 1$–4) are marked at 3565, 3400, 3240 and 3080 cm^{-1}, respectively (resolution = 4 cm^{-1}).