Supplemental Material

Dielectric barrier discharge plasma-assisted hydrogen diffusion flame. Part 1: temperature, oxygen, and fuel measurements by one-dimensional fs/ps rotational CARS imaging

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Complications with the O2/N2 measurements at long probe delays revolve around spectroscopic complexities introduced by the triplet character of the ground electronic state of O2. In this case, 2*S* + 1 = 3, or *S* = 1, where *S* is the electron spin. The angular momentum for the molecule is then described by rotational, *N*, and total angular momentum, *J*, quantum numbers, where *J* = (*N* − 1, *N*, *N +* 1). For a rotational Raman transition with *N* = +2, which contributes the CARS spectrum, the selection rules are *J* = 0, ±1, ±2, so that the coupling of the electronic and nuclear angular momenta splits the Raman transition into six possible lines, as describe by Berard *et al*. [1] and shown in Figure S1. The transitions are grouped and denoted as (*S*−, *S*0, *S*+), with these main groupings separated by nominally ~2 cm−1, and a much finer splitting between the three transitons which compose the *S*0 group. The splitting between these three groups leads to both high- and low-frequency beats in the time-dependent O2 Raman polarization, which impact the dephasing of the Raman coherence and are not captured by the single exponential decay of Eq. 1 in the main paper.

 

Fig. S1. (a) Energy level diagram for the 6 possible transitions for the N = 1 to N = 3 case and (b) the corresponding lines in the frequency domain using the calculated line strengths. Figures are obtained from information in Berard *et al.* [1].

(a)

(b)

We have simulated the O2 coherence decay, probed by Gaussian pulses of 5 ps and 60 ps FWHM. Transition data from Berard *et al.* [1] were used with expressions similar to Eqs. 1-4 in our paper, where we consider a single Raman transition from *N* to *N′* = *N* + 2, and the summation is taken over all 6 possible (*N,J*) combinations. Simulated decays for *N* =1 and *N* = 9 are shown in Figure S2. A short, 5-ps-duration probe pulse, resolves both the high- and low-frequency beat contributions for the *N* = 1 Raman transition. The period of the high-frequency beat is ~17 ps has been observed experimentally by Miller *et al.* [2] for the *N* = 1 and 3 transitions in O2. At *N* = 9, the transition strength of the *S*− and *S*+ groupings is weak, and no high-frequency beat is observed. The low-frequency beat contribution has much more significant impact on practical measurements using hybrid fs/ps CARS. This contribution is effectively a sinusoid superposed with an exponential decay, such that the Raman polarization is dephased more rapidly than the simple exp(−*Jt*) alone.

 

Fig. S3. (a) Signal decay for the N = 1 Raman transition, demonstrating high frequency beating when probed with a short probe pulse (integrated over otherwise) and (b) the signal decay for the N = 9 Raman transitions, demonstrating minimal high frequency content.

(a)

(b)

Our coherence-decay measurements acquired from H2/air flames stabilized on the Hencken burner are shown in Figure S3 for the indicated isolated O2 lines at probe delays ranging from ** 100 to 450 ps. The coherence decay data in Figure S3(b) indicate the first half period of the beat, which increases with *N* and is approaching ~1 ns for N = 11-29. The simulated coherence dephasing of Figure S3 has been bserved experimentally by Courtney *et al*. [3], and it is this long-duration beating is the source of the unexpectedly rapid decay of the O2 Raman polarization in our experiments.

 

Fig. S1. (a) Average spectrum taken at 920 K in the Hencken burner with isolated O2 lines marked and (b) their corresponding signal decay as a function of probe delay demonstrating the beginning of the low-frequency beating of the fine-split O2 transitions in the *S0* triplet.

(a)

(b)

[1] M. Bérard, P. Lallemand, J.P. Cebe, M. Giraud, Experimental and theoretical analysis of the temperature dependence of roatational Raman linewidths of oxygen, Journal of Chemical Physics 78 (1983) 672-687.

[2] J.D. Miller, S. Roy, J.R. Gord, T.R. Meyer, Time-Domain Measurement of High-Pressure N2 and O2 Self-Broadened Linewidths Using Hydrid Femtosecond/Picosecond Coherent Anti-Stokes Raman Scattering, Journal of Chemical Physics 135 (2011) 201104.

[3] T. Courtney, B. Pattterson, C.J. Kliewer, Time-resoived decay of the rotational Raman coherence in O2, Journal of Chemical Physics (submitted), (2017).