Appendix V.

COMMENTS ON "LASER-EXCITED FLUORESCENCE OF THE HYDROXYL RADICAL: RELAXATION COEFFICIENTS AT ATMOSPHERIC PRESSURE"

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The reported results of Chan et al do not support their contention that the quenching cross sections due to oxygen are pressure dependent. Discrepancies among their own results are also noted.

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The lifetime of the excited state of an atom or molecule can often be determined from the rate of fluorescence decay originating from the excited state. By measuring this fluorescence lifetime as a function of buffer gas pressure, an accurate determination can be made of the rates of collision-induced transitions away from the excited state. In the case of the hydroxyl radical (OH), direct lifetime measurements have been made over a range of low system pressures up to about 25 torr.[1-5] However, attempts to extend this type of measurements to atmospheric pressure have been met with increasing difficulty since excitation and detection with subnanosecond resolution are required. Recently, Chan et al[6] reported measurements near atmospheric pressure using a 7-nanosecond laser for excitation, concluding that a strong pressure dependence existed for the electronic quenching cross section of OH due to oxygen. They also stated that this pressure dependence would mean a factor of ten error in the OH concentrations deduced from fluorescence measurements in ambient air, a topic of considerable interest to us. The purpose of this comment is to point out that their reported results do not support their conclusion, and that the results themselves do not appear to be internally consistent. On the other hand, various observations published in the last ten years by a number of other independent workers[1-4,7] all tend to support the supposition that pressure dependence at atmospheric pressure is negligible for the quenching and relaxation cross sections of OH. In view of these considerations, we do not believe the conclusions reached by Chan et al are valid.

The success of any measurement of fluorescence lifetime is predicated upon the use of an exciting laser and detection electronics both of which are fast compared to the fluorescence lifetime to be measured. This point is brought to light in the earlier publications. For example, an accurate determination of the fluorescence lifetime in Eq. (6) or Eq. (7) of Ref. 6 would not be possible when the fluorescence lifetime to be determined is much shorter than the pulsewidth of the exciting laser and/or the resolution time of the detection electronics. The data which led Chan et al to claim the existence of a pressure dependence were presumably taken in oxygen at pressures of 40 torr and higher. At 40 torr, as may be deduced from the results in their Fig. 8, the fluorescence lifetime is already shorter than their laser pulsewidth by a factor of about 35. This being the case, the temporal shape of the fluorescence signal would be insensitive to the value of the fluorescence decay rate, so that any value deduced from the temporal shape would at best be inaccurate. It thus follows that these authors need to improve their temporal resolution by about an order of magnitude in order to make meaningful measurements of the fluorescence lifetime of OH at 40 torr of oxygen. For measurements at higher pressures, still faster excitation and detection will be necessary. In our opinion, the results of Chan et al represent a commendable attempt at a difficult but important problem in atmospheric chemistry, but their statement that "a ... strong ... pressure dependence was found ..." appears to be premature and unwarranted.

According to the conjecture outlined by Chan et al, resonant energy transfer with oxygen molecules should lead to enhanced electronic quenching rate for the excited state OH in the v' = 1 manifold, but not for the excited state OH in the v' = 0 manifold. In the limit of small radiative decay rate, one would expect from their Eq. (21) that the ratio of the fluorescence intensities near 3,909Å and 3,140Å should remain the same at atmospheric pressure as that observed previously at lower pressures. Furthermore, this ratio should also remain the same even in the absence of any resonant enhancement of the quenching rate. This analysis suggests an error in their results of Fig. 10, which show a ratio at atmospheric pressure that is four times larger than the ratio at lower pressures.

The question of pressure dependence for the quenching cross sections of OH is obviously an important one as it affects the value of OH concentrations deduced from fluorescence measurements. As was discussed at length in Ref. 5, the quenching cross sections due to nitrogen and oxygen are independent of pressure up to 25 torr, and will most probably remain so up to atmospheric pressure. This conclusion was based on the fact that no pressure dependence was observed either in direct lifetime measurements at lower pressures [1-5] or in Stern-Volmer type measurements[7] up to atmospheric pressure. It also agrees well with other theoretical and experimental considerations such as the pressure independence of the observed fluorescence spectrum, and the estimated magnitude of any possible pressure dependence at atmospheric pressure. In view of these results and the difficulties associated with the experiments of Chan et al, we believe it is prudent to assume that the quenching cross sections of OH are pressure independent at atmospheric pressure.

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Note added in proof:

Based on their reply to this comment, it is my understanding that Drs. Chan et al agreed with me on my position as outlined in my introductory paragraph, but insisted that the temporal resolution of their detection system was as good as 0.2 nsec. I have no trouble in agreeing that deconvolution can in principle be employed to resolve fluorescence times shorter than the response times of the system. However, attainable reproducibility and accuracy in actual experiments usually set a limit beyond which no meaningful results can be expected from deconvolution processes. Just how restrictive this limit may be is also difficult to evaluate. Prudence thus dictates that the results of deconvolution be viewed with extreme caution whenever fluorescence times much shorter than the response times of the system are indicated.

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