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Short Communication

The pressure dependence of the fluorescence quenching of NO_2^*

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Recently a paper by Birnbaum *et al.* [1] has appeared in which it is reported that the quenching of the fluorescence of electronically excited NO_2 (NO_2^*) produced with 441.6 nm radiation followed a Stern–Volmer law (with up to 1 atm of N_2 or air as a quenching gas). An earlier report by Braslavsky and Heicklen [2] had indicated very marked deviations from Stern–Volmer quenching at pressures in excess of a few torr. Thus Birnbaum *et al.* [1] concluded that the two sets of results disagreed. It is the purpose of this paper to show that there is not necessarily a conflict between the studies.

There was an important experimental difference between the two studies in addition to the different pressure ranges that were examined. Birnbaum *et al.* [1] collected all the fluorescent radiation, whereas Braslavsky and Heicklen [2] monitored the fluorescent radiation at a single wavelength (486.0, 557.7 or 630.0 nm). This difference in the two experiments could be the reason for the apparent discrepancy.

The mechanism utilized by Braslavsky and Heicklen [2] to explain their results was

$$NO_2 + h\nu \rightarrow NO_2^* \quad (1)$$

$$NO_2^* \rightarrow (NO_2^{**})_n \quad (2a)$$

$$\rightarrow NO_2 \quad (2b)$$

$$NO_2^* + NO_2 \rightarrow 2NO_2 \quad (3)$$

$$NO_2^* + M \rightarrow NO_2 + M \quad (4)$$

$$(NO_2^{**})_n \rightarrow NO_2 (+ h\nu) \quad (5)$$

$$(NO_2^{**})_n + NO_2 \rightarrow (NO_2^{**})_m + NO_2 \quad (6a)$$

$$\rightarrow 2NO_2 \quad (6b)$$

$$(NO_2^{**})_n + M \rightarrow (NO_2^{**})_m + M \quad (7a)$$

$$\rightarrow NO_2 + M \quad (7b)$$

$$(NO_2^{**})_m \rightarrow NO_2 + h\nu \quad (8a)$$

$$\rightarrow NO_2 \quad (8b)$$

$$(NO_2^{**})_m + NO_2 \rightarrow 2NO_2 \quad (9)$$

$$(NO_2^{**})_m + M \rightarrow NO_2 + M \quad (10)$$

where M is a foreign quenching gas, the superscripts * and ** represent two different electronically excited levels and the subscripts n and m represent vibrational excitation. The state $(NO_2^{**})_m$ represented the lowest level energetically capable of producing a photon that could be detected at a specified emission wavelength. It was not intended to imply that emission could not occur in reactions (2b) or (5), or from the NO_2 molecules produced in reactions (6b), (7b), (9) and (10). The mechanism was written as above to indicate that the bulk of the observed emission came from reaction (8a). In fact NO_2^* must emit to some extent since it is formed by the absorption of radiation.

If reactions (6b), (7b), (9) and (10) produce ground vibrational state NO_2^{**} molecules which can emit radiation, this radiation would not have been seen by Braslavsky and Heicklen [2] and their rate law would remain unchanged. However, the radiation from the ground vibrational level of NO_2^{**} would have been seen by Birnbaum *et al.* and the predicted rate law would be Stern–Volmer as observed:

$$Q_f^{-1} = \frac{k_2 + k_3 [NO_2] + k_4 [M]}{k_{2a} f}$$

where Q_f is the fluorescence efficiency and f is the ratio of fluorescence to total first order loss processes for NO_2^{**}.

Most investigators, including Birnbaum [3], accept the model with two electronically excited states. Thus, for Stern–Volmer quenching to occur one of the electronically excited states must be collisionally quenched, whereas the other cannot be. Further evidence that at least one of the electronically excited states is not primarily collisionally quenched to the electronic ground state comes from the fact that the fluorescence spectrum shifts with pressure [4]. This indicates primarily vibrational quenching on collision for at least one of the excited electronic levels.

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3 M. Birnbaum, personal communication, 1977.
M. Birnbaum, in E. L. Wehry (ed.), Modern Fluorescence Spectroscopy, Vol. 1, Plenum Press, New York, 1976, Chap. 5.
4 G. H. Myers, D. M. Silver and F. Kaufman, J. Chem. Phys., 44 (1966) 718.