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[18] J. Derouard, R. Jost, M. Lombardi, T. A. Miller, and R. S. Freund, Phys. Rev. A 14, 1025 (1976).

[19] T. A. Miller and R. S. Freund, Adv. Mag. Reson. (in press).

[20] F. A. Jenkins, Phys. Rev. 31, 539 (1928).

[21] J. E. Rosenthal and F. A. Jenkins, Proc. Natl. Acad. Sci. (USA) 15, 381 (1929).

[22] G. Herzberg and A. Lagerqvist, Can. J. Phys. 46, 2363 (1960).

[23] V. E. Bondybey and L. E. Brus, J. Chem. Phys. 63, 2223 (1975).

The laser-stimulated reaction*: $NO_2^* + CO \rightarrow NO + CO_2$

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This letter reports the observation of the room temperature gas phase reaction of NO_2, excited by various cw visible lasers, with CO to form NO and CO_2, in which the CO_2 product is detected by laser-induced fluorescence with a CO_2 laser. Previously, this reaction has been observed only at elevated temperatures, $T > 225$ °C.[1]

In a typical run 2 torr of purified NO_2 is mixed with 4 torr CO and is irradiated with one of the available wavelengths from an argon-ion laser ($\lambda = 4579$–5145 Å) for 15 min or a Rhodamine 6*G* dye laser[2] ($\lambda = 5786$–6125 Å) for 2 h. Afterwards, the CO_2 product, having partial pressure on the order of 1 mtorr, is distilled from the reactants and other products and is mixed with a background buffer of argon at 850 mtorr. A cw CO_2 laser, chopped at 338 Hz, oscillates at the $P(16)$ (10 °0) → (00 °1) transition, $\lambda = 10.55$ μ, and excites hot band CO_2 molecules in $J = 16$ (10 °0) to $J = 15$ (00 °1) which can then radiate 4.3 μ photons and relax to the ground vibrational state (00 °0). The fluorescence is measured by phase-sensitive detection using an InSb photovoltaic detector, with sapphire window, which is blind to background laser scatter. The addition of the argon buffer both increases the fluorescence by an order or magnitude over that of the pure CO_2 product, because of reduced diffusion of excited CO_2 to the walls, and makes the fluorescence signal linearly proportional to the CO_2 concentration. These quantitative determinations were made by absolute calibration of the CO_2 fluorescence with known amounts of CO_2 in argon background.

Experiments with 4880 Å radiation show that CO_2 production is linear with the duration of irradiation and that the rate of reaction is linear with incident visible power, indicating that the reaction is nonthermal. The effects of NO_2 photodecomposition[3] are of minor importance under experimental conditions. The dependence of the rate of reaction with reactant pressure is in agreement with a mechanism consisting of bimolecular reaction of NO_2^* (reactive NO_2) with CO, first order in each, where the NO_2^* population is determined by the steady-state balance of laser absorption and collisional relaxation by NO_2 and CO. At the pressures of interest radiative relaxation is very slow compared to collisional decay.[4,5]

Figure 1 shows that the reaction rate constant increases rapidly with the laser photon energy. The plotted data are obtained by dividing the observed laser-induced fluorescence signal, which is proportional to the CO_2 concentration, by the average absorbed laser power and by the duration of irradiation; it is therefore corrected for the wavelength dependent absorption coefficient and laser power and for the longer irradiation times required with dye laser excitation. Because of collisional relaxation these data actually represent an average of the reaction rate constants of the various excited NO_2 states each weighted by its population.

Using the mechanism described above the rate of production of CO_2 is

$$\frac{d[CO_2]}{dt} = A \frac{k_R [NO_2][CO]}{\gamma_{NO_2}[NO_2] + \gamma_{CO}[CO]},$$

where k_R is this average reaction rate constant, γ_{NO_2} and γ_{CO} are the average rates of relaxing NO_2^* to a non-

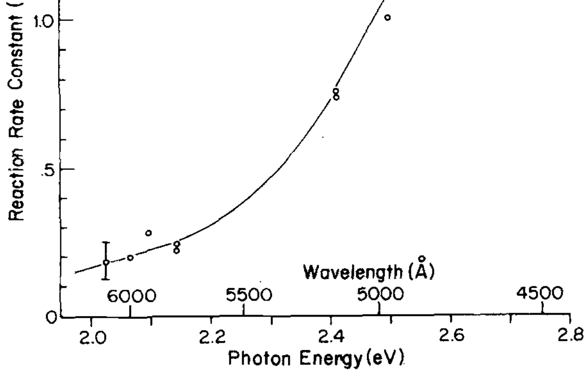

FIG. 1. The reaction rate constant is plotted as a function of the exciting wavelength. It has been normalized for laser power, NO_2 absorption coefficient, and the duration of irradiation as described in the text.

reactive state by NO_2 and CO, respectively, and A is proportional to the laser power and the NO_2 absorption coefficient (when the sample is optically thin) and is also dependent on the reaction cell geometry. Preliminary analysis of these data indicates that with 4880 Å irradiation k_R/γ_{NO_2} is 2.0×10^{-5}, with an estimated 40% experimental accuracy. The quantity $\gamma_{CO}/\gamma_{NO_2}$ has been set equal to 0.57. This ratio was determined by measuring the fluorescence intensity of 4880 Å excited NO_2 as a function of $[NO_2]$ and $[CO]$ using a 1P28 photomultiplier preceded by a Wratten #12 filter (net spectral sensitivity $\lambda = 5100-6000$ Å). The fluorescence intensity varies as the rate of exciting NO_2 to an excited electronic state, proportional to $[NO_2]$, divided by the relaxation rate, $\gamma_{NO_2}[NO_2]+\gamma_{CO}[CO]$.[6] While k_R/γ_{NO_2} is basically an experimentally determined quantity, the value obtained for k_R, however, depends on the kinetic scheme employed.

If it is assumed that the NO_2 reactive states are also the states that fluoresce, then γ_{NO_2} can be equated to the rate of relaxation of NO_2 visible fluorescence. By measuring the decay of visible fluorescence integrated from the exciting wavelength, 4880 Å, to about 7500 Å in pure NO_2, Sakurai and Broida[4] measured $\sigma^2\tau_{rad}$, where σ is the collision diameter and τ_{rad} is the radiative lifetime. Using $\tau_{rad} = 70$ μsec[5,7] approximately 1 in 20 collisions of NO_2^* and NO_2 deactivate the NO_2^*. From this and the measured value of k_R/γ_{NO_2} one obtains $k_R = 2.2\times10^{-16}$ cc/molecule sec, corresponding to a reaction in only 1 in 10^6 collisions of excited NO_2 and CO. If, instead, γ_{NO_2} is equated to the decay rate of the 5050–5070 Å continuum fluorescence,[4] the calculated reaction rate constant is $k_R = 1.2\times10^{-15}$ cc/molecule sec. Though this reaction is fairly slow it is still much faster than the thermal rate at room temperature.

Laser-induced fluorescence experiments of NO_2 [8] imply that the $^2B_2$ and, to a much lesser degree, the $^2B_1$ excited electronic states are directly populated by the laser, however, upon collision there is probably strong mixing of these states with high lying vibrational levels of the ground electronic state $X(^2A_1)$.[5] Inspection of the correlation diagrams relating the electronic states of the reactants and the products suggests that it is the $^2B_2$ state that is the reactive species. Since most fluorescence originates from NO_2 in the $^2B_2$ state, the assumptions relating γ_{NO_2} and decay of fluorescence are, in part, justified.

Further experimental details and a more complete discussion of the reaction dynamics and the fluorescence detection scheme will be published shortly.

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[1] F. B. Brown and R. H. Crist, J. Chem. Phys. 9, 840 (1941). H. S. Johnston, W. A. Bonner, and D. J. Wilson, J. Chem. Phys. 26, 1002 (1957).

[2] We wish to thank Coherent Radiation for the loan of their model 590 dye laser.

[3] C. L. Creel and J. Ross, J. Chem. Phys. 64, 3560 (1976).

[4] K. Sakurai and H. P. Broida, J. Chem. Phys. 50, 2404 (1969).

[5] S. E. Schwartz and H. S. Johnston, J. Chem. Phys. 51, 1286 (1969).

[6] The experimentally determined efficiency of CO quenching fluorescence in a given bandwidth, relative to that of NO_2, increases somewhat as the center wavelength of the bandwidth decreases.

[7] P. B. Sackett and J. T. Yardley, J. Chem. Phys. 57, 152 (1972).

[8] K. Abe, F. Myers, T. K. McCubbin, and S. R. Polo, J. Mol. Spectrosc. 38, 552 (1971); K. Abe, *ibid.* 48, 395 (1973); W. Demtröder, F. Paech, and R. Schmiedl, Chem. Phys. Lett. 26, 381 (1974); R. E. Smalley, L. Wharton, and D. H. Levy, J. Chem. Phys. 63, 4977 (1975); C. G. Stevens and R. N. Zare, J. Mol. Spectrosc. 56, 167 (1975).

Microwave double resonance spectrum of OCS in the $v_2 = 1$ state: Observation of non-dipolar collision-induced transitions*

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In recent microwave double resonance studies[1,2] of collisional population transfer among rotational levels of the ground vibrational state of OCS, the rates of non-dipolar $\Delta J = 2$ parity $\pm \leftarrow \pm$ collision-induced transitions were found to be surprisingly large compared to those for the $\Delta J = 1$ parity $\pm \leftarrow \mp$ dipole-type transitions. In view of the formidable body of experimental and theoretical work on collisional broadening and relaxation in OCS,[3] any new information on the collisional pathways is of some importance. We have therefore extended the study to the first excited state of the bending vibration, $v_2 = 1$, in which the l-doubling of the rotational levels leads to a significant increase in the number and variety of collisional channels possible. Here, for the $(3 \leftarrow 2)_s - (2 \leftarrow 1)_s$ system, we report some novel and interesting features which provide further strong evidence for the

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