1474 (1960).

[3] While H^* is used mainly to simplify the analytical expressions, physically it is the field that must be applied to the specimen in excess of the bulk critical field in order that critical currents may be induced to flow through the entire specimen. In other words, the penetration depth Δ is equal to the radius R when this condition obtains.

[4] C. Chou, D. White, and H. L. Johnston, Phys. Rev. 109, 788 (1958).

[5] A. A. Abrikosov, J. Exptl. Theoret. Phys. (U.S.S.R.) 32, 1442 (1957) [translation: Soviet Phys.—JETP 5, 1174 (1957)].

[6] B. B. Goodman, Phys. Rev. Letters, 6, 597 (1961).

[7] A. B. Pippard, Trans. Roy. Soc. (London) A248, 97 (1955).

INFRARED RESONANCE FLUORESCENCE IN THE FUNDAMENTAL VIBRATION-ROTATION BAND OF CARBON MONOXIDE*

Roger C. Millikan
General Electric Research Laboratory, Schenectady, New York

(Received February 21, 1962)

The collisional deactivation of vibrationally excited diatomic molecules is known to be a slow process at low temperatures. Indeed, for carbon monoxide gas at 300°K and one atmosphere pressure, a time constant of five seconds is indicated by extrapolating the vibrational relaxation data of Matthews[1] and of Hooker.[2] A long extrapolation is required, however, since those shock tube data cover the 4900-1100°K range. In contrast, the radiative lifetime of vibrationally excited CO deduced from absorption measurements is 0.03 second.[3,4] If the extrapolation is valid, then at room temperature the loss of vibrational excitation by radiation should be 160 times faster than loss by collision. This suggested that an infrared fluorescence experiment would be possible if the deactivating effect of impurities and wall collisions could be avoided. This note reports the results of such an experiment.

We have observed fluorescence of carbon monoxide gas (300°K, 1 atm) in its fundamental vibration-rotation band centered at 2143 cm^{-1}. The problem of wall collisions was eliminated by using an "open-air" flow system in which the CO sample was contained in a surrounding flow of argon. We have found that CO-Ar collisions are less effective in deactivating vibrationally excited CO molecules than are CO-CO collisions.

Carbon monoxide (Matheson, cp grade), obtained from a tank through pressure regulators and a critical orifice flowmeter, was passed through two cold traps, one at -80°C and one at -150°C, for purification. The gas issued from a 3.5-cm diam porous disk with a laminar flow velocity of 10 cm/sec. This flow of CO was surrounded by a 1.2-cm wide annular argon flow of matched velocity. The composite stream was illuminated 2 cm above the gas ports from two opposing sides with collimated light from 2500°K zirconia sources. The infrared fluorescence was observed in the same plane, but at right angles to the beams of exciting light with an infrared spectrometer set to accept the entire 1900 to 2300 cm^{-1} region. The response of the spectrometer was calibrated by keeping the exciting lights off and thermally heating the gas flow with hot water coils imbedded in the porous disks. A gas temperature rise of 2°C was detectable with a signal-to-noise ratio of unity. When the exciting lights were turned on, a signal was observed equivalent to a 30°C gas temperature rise. Convincing evidence that the exciting lights were heating the gas 30°C in a nonequilibrium fashion was obtained by warming the second cold trap in the CO line from -150°C to -120°C. This permitted one percent of CO_2 to enter the gas stream. The signal vanished. Recooling the trap to -150°C restored the signal. This quenching of the signal by impurities shows that we are observing fluorescence, for equilibrium emission from the CO, or even scattered light, would not be so affected.

The radiative lifetime of the first excited vibrational state of CO has been determined by exciting the flowing CO stream at one position, and measuring the decay of the fluorescence at several points downstream. For known flow velocities the elapsed time between excitation and detection is easily calculated. For pure CO we found that the decay of the fluorescence was nearly exponential, but the deduced time constant was over four times the value given by absorption intensity measurements.[3,4] Suspecting that the

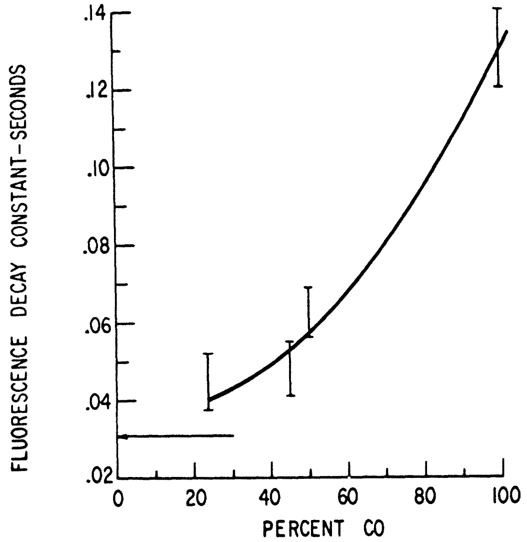

FIG. 1. Time constant for decay of $1\rightarrow 0$ vibrational fluorescence in carbon monoxide against percent CO in the CO-Ar stream. →: Radiative lifetime for the $1\rightarrow 0$ vibrational transition in CO from reference 3.

resonance fluorescence was being imprisoned by reabsorption, we began to dilute the central flow of CO with argon. As the CO flow was progressively diluted, the decay curves became better straight lines on semilog plots, and the measured lifetime dropped toward the previously known value as shown in Fig. 1. Unfortunately, as the CO was diluted, the signal-to-noise ratio suffered, and it was not possible to go beyond the 25% CO-75% Ar point. Even so, we have come within 30% of the 0.03-second lifetime found by others.

In pure CO where the fluorescence is trapped, we have detected it as far as 4 cm or 0.2 second past the point of excitation. Since the classical collision rate for our conditions is of the order of 10^{10} sec^{-1}, this means that a measurable fraction of the vibrational excitation has survived more than 10^9 collisions without being converted to translational or rotational energy. This finding is consistent with the extrapolation of shock tube data mentioned earlier. The effect of impurities upon such a long collisional lifetime is pronounced. Nearly all polyatomic species, and especially water molecules, are effective collision catalysts for the transfer of vibrational energy.

This observation of vibrational fluorescence in CO makes possible a number of experiments that can critically test current theories of vibrational relaxation. The quenching effect of impurities can also serve as a tool for studying small chemical affinities in collisions of carbon monoxide with other molecules.

The author thanks L. A. Osburg and W. I. Foss for help with the experimental work. Helpful discussions with Dr. Marshall Lapp aided this work considerably.

---

*This work was supported in part by the U. S. Air Force, Ballistic Systems Division.

[1] D. L. Matthews, J. Chem. Phys. 34, 639 (1961).

[2] W. J. Hooker (private communication).

[3] S. S. Penner and D. Weber, J. Chem. Phys. 19, 807 (1951); 19, 974 (1951).

[4] J. Vincent-Geisse, Ann. phys. 10, 693 (1955).