Quenching of CO(B $^1\Sigma^+$, $v=0$) by He, Ne, Ar, H$_2$ and D$_2$

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Excitation of CO molecules into the lowest vibrational level of the B $^1\Sigma^+$ electronic state by absorption of the (B $^1\Sigma^+$, $v'=0 \to$ X $^1\Sigma^+$, $v''=0$) resonance band at 1150 Å has been studied under various experimental conditions by observing the steady state fluorescence of the (B $^1\Sigma^+ \to$ A $^1\Pi$) Angstrom bands. Stern-Volmer plots of the fluorescence intensities at the addition of various foreign gases yielded straight lines whose slopes $\widetilde{k^q_M} = k^q_M \cdot \tau_{\text{eff}}$ were strongly dependent on the CO sample pressure. This effect was found to be due to changes of the effective radiative lifetime of the B $^1\Sigma^+$, $v'=0$ because of resonance trapping of the (0, 0) band of the (B $\to$ X) fluorescence. The CO(B $^1\Sigma^+$, $v'=0$) molecules are found to be quenched by He, Ne, Ar, H$_2$ and D$_2$ with effective collision cross sections of 0.23, 0.48, 22.4, 10.7, and 11.4 Å^2, respectively, at 298 °K. In addition, an approximate value for the ratio A$_{BA}$/(A$_{BA}$+A$_{BX}$) of the radiative transition probabilities of the (B $\to$ A) and (B $\to$ X) transitions could be derived from the measurements.

Introduction

Measurements of the collisional deactivation of electronically excited molecules in well defined vibrational quantum states imply a mode of excitation which populates only a single vibrational level of the electronic state. This is usually achieved by optical excitation of molecules through resonance absorption of atomic lines which happen to coincide with one of the molecular absorption lines. This method has been applied to many diatomic molecules including I_2 [1], NO [2, 3], HD [4], Li_2 [5], and CO [6]. Recently, we have shown that in favorable cases molecular resonance bands which are filtered out of the complex emission spectrum of a suitable light source by a monochromator may be used to excite systematically the different vibrational levels of electronically excited molecular states to study collisional relaxation and quenching processes [7, 8]. Through resonance absorption of CO(A $^1\Pi$, $v' \to$ X $^1\Sigma^+$, $v''=0$ fourth positive bands CO molecules were excited selectively into the levels $v'=0$ to $v'=8$ of the A $^1\Pi$ state. By studying the (A $\to$ X) fuorescence spectra at the addition of foreign gases cross sections for the vibrational relaxation and quenching of CO(A $^1\Pi$) molecules in 9 different vibrational levels could be obtained.

In this paper we report the application of this excitation method to measure the effective quenching cross sections for collisions of CO molecules in the lowest vibrational level of the B $^1\Sigma^+$ state with various rare gas atoms and hydrogen molecules. Selective excitation of the B $^1\Sigma^+$, $v'=0$ state was achieved by resonance absorption of the CO(B $^1\Sigma^+$, $v'=0 \to$ X $^1\Sigma^+$, $v''=0$) band. The (B $\to$ X) system belongs to the so-called Hopfield-Birge systems of the CO molecule. The equilibrium internuclear distance and the vibrational quanta of the B $^1\Sigma^+$ state are very close to the corresponding values of the X $^1\Sigma^+$ ground state [9]. This strongly favours the Franck-Condon overlap integrals of the $\Delta v = 0$ bands of the (B $\to$ X) transition. The Franck-Condon factor of the (0, 0) band, for instance, has been calculated to be 0.988 [10]. As a result, the (B $\to$ X) system consists mainly of a sequence of $\Delta v = 0$ bands near 1150 Å. These bands are not as well known as the previously studied (A $\to$ X) system which is the most prominent band system of CO in the ultraviolet and vacuum-u. v. regions. However, the (B $\to$ X) emission is also readily obtained from a microwave discharge through a mixture of CO_2 and He. The intensity of the unresolved $\Delta v = 0$ sequence emitted from this light source is about a factor of 10 lower than that of the strongest (A $\to$ X) bands.

In addition to the (B $\to$ X) transition the B $^1\Sigma^+$ state can be depopulated by radiation to the A $^1\Pi$ state. The (B $\to$ A) transition is well known as the Ångstrom system. The Ångstrom bands mainly cover the wavelength region between 4100 and 6000 Å and, therefore, can easily be used to measure the B $^1\Sigma^+$ state population.

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The $(0, 0)$ band of the $(B \rightarrow X)$ vacuum-u. v. fluorescence is strongly reabsorbed by non-excited ground state molecules. Due to the large Franck-Condon factor of the $(0, 0)$ band, resonance trapping of the vacuum-u. v. fluorescence light leads to a dependence of the effective lifetime of the $B\,^1\Sigma^+$, $v' = 0$ state on the CO sample pressure. This effect has been demonstrated by Moore and Robinson [11] in lifetime measurements of the $B\,^1\Sigma^+$, $v' = 0$ state. According to their measurements the effective radiative lifetime of this state varies from the "natural" lifetime of about 22 nsec [12, 13] at very low CO pressures to values of $65 - 75$ nsec at the limit of total trapping of the $(B\,^1\Sigma^+, v' = 0 \rightarrow X\,^1\Sigma^+, v'' = 0$ emission where the radiative depopulation is mainly by the emission of the Ångstrom bands.

In the present work the effect of resonance trapping of the $(B \rightarrow X)$ fluorescence radiation on the quenching of $CO(B\,^1\Sigma^+, v' = 0)$ was studied in detail. The quenching constants $k_M^q = k_M^q \cdot \tau_{eff}$ obtained from Stern-Volmer plots of the relative fluorescence intensity as a function of added gas pressure showed a strong dependence on the CO sample pressure which reflects the variation of τ_{eff} due to the changing degree of resonance trapping. The quenching constants at very low CO pressure together with the known natural lifetime of the $B\,^1\Sigma^+$ state yielded effective cross sections for the deactivation of $CO(B\,^1\Sigma^+, v' = 0)$ molecules in collisions with different rare gas atoms and hydrogen molecules. In addition, the ratio $A_{BA}/(A_{BA} + A_{BX})$ of the transition probabilities of the $(B \rightarrow A)$ and $(B \rightarrow X)$ transitions was obtained from the measurements.

Experimental

Two different types of experiments were carried out to identify and measure the fluorescence radiation from CO excited by absorption of $(B \rightarrow X)$ bands. In both cases the primary excitation source was a microwave discharge through a CO_2/He mixture. This same light source has been used in preceeding experiments to excite CO to its $A\,^1\Pi$ electronic state [7, 8]. The lamp was equipped with either a LiF or a MgF_2 window resulting in short wavelength cut-offs at 1050 Å and 1130 Å, respectively.

In the first type of experiment the total output of the lamp was introduced into a pyrex fluorescence cell of 5 cm diameter and 10 cm length ending in a Wood's light trap. The fluorescence radiation was measured at right angles to the primary light beam with a monochromator (McPherson Model 218, grating: 600 lines/mm, blazed for 5000 Å) and a photomultiplier (RCA Type C 31000 D). The detector was connected to a pulse circuitry, a digital-analog converter, and a chart recorder.

In the other type of experiment we made use of a vacuum monochromator (McPherson Model 225, grating: 1200 lines/mm, blazed for 1500 Å) for dispersing the radiation from the light source in order to excite the fluorescent medium only by the $(B, v' = 0 \rightarrow X, v'' = 0)$ emission at 1150 Å. A T-shaped fluorescence cell made from stainless steel was mounted at the excit slit housing of the monochromator. The photomultiplier monitored the total visible fluorescence light at right angles to the primary light beam which entered the cell through a LiF window.

This set-up reduced the stray light problem substantially. A small amount of stray light, still present from the bright lamp, was completely suppressed by placing an interference filter with a center wavelength near the $(0, 1)$ band of the Ångstrom system ($\lambda_0 = 4850$ Å, half-width = 100 Å) in front of the photomultiplier tube.

Typical operating conditions for the microwave lamp were a helium pressure of 0.1 to 0.2 torr with about 50 mtorr of CO_2. But sometimes total pressures up to several torr were used in order to check the independence of the results upon the lamp conditions. The power generator was usually set at 40 watts. The pressure in the lamp and the CO pressure in the fluorescence cell were controlled by Pirani gauges. A McLeod manometer was used for absolute measurements of the CO pressure. The pressure of the added gases was measured with either a capacitor manometer or a mercury torrmeter. All gases used were Air Liquide "High Purity" grade with total impurities in the ppm range.

Results

The measurements were started by analysing the fluorescence emission in the visible between 4000 and 6000 Å when the total emission of the light source was irradiated into the fluorescence cell containing CO at pressures between 1 and 100 mtorr. Figure 1 (upper trace) shows that the major emissions which appear in this wavelength region are the $(0, 0)$, $(0, 1)$, $(0, 2)$, and $(0, 3)$ bands of the Ångstrom system of CO at 4510.9, 4835.2, 5198.2, and 5610.2 Å, respectively [9]. With a MgF_2 window the $B\,^1\Sigma^+$, $v' = 0$ level is the highest level that is energetically accessible. But even when a LiF window

was used no Ångstrom bands from vibrational levels $v' > 0$ could be observed. This is to be expected since the intensities of the $(v' > 0, v'' = 0)$ bands emitted from the light source were much lower than that of the (0, 0) band. In addition, due to the small Franck-Condon factors of all bands with $\Delta v \neq 0$, the absorption coefficients of the $(v'' = 0, v' \neq 0)$ absorption bands are much smaller than that of the (0, 0) band. Figure 1 shows that besides the Ångstrom bands only weak emissions of triplet transitions occur [14]. Most of the light underlying the Ångstrom bands is straylight from the microwave lamp, as indicated by the lower trace in Fig. 1 which shows a spectrum without CO in the fluorescence cell.
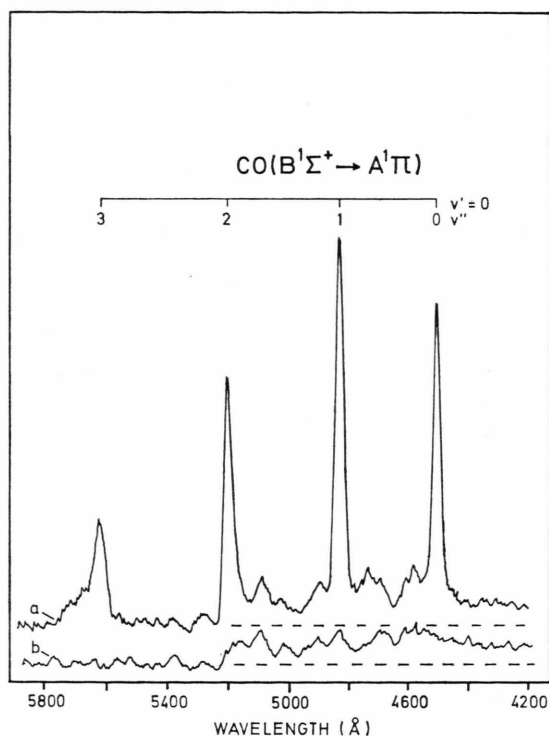

Fig. 1. Fluorescence spectrum of CO excited by a CO$_2$/He microwave discharge lamp; trace a: $p_{CO} = 50$ mtorr, trace b: straylight spectrum.

As already mentioned, stray light problems could be very effectively suppressed by using the second type of the experimental set-up. In this case only the $\Delta v = 0$ sequence at 1150 Å was irradiated into the fluorescence cell. Although preliminary quenching measurements were made with the first type of experimental set-up, all further experiments were carried out with the second one.

When using radiation to excite atomic or molecular states for the purpose of quenching measurements great care has to be given whether the addition of the quenching gas has an influence on the absorption properties of the absorber. In previous work when molecules were excited by resonance absorption of atomic lines it has been found that due to pressure broadening of the absorption lines the overall absorption in the fluorescence cell strongly increased when foreign gases were added to the absorbing gas [2, 4]. As a result, Stern-Volmer plots of the fluorescence intensities did not lead to straight lines, and it was difficult to deduce quenching efficiencies from such measurements. However, in our previous studies of the quenching of (A $^1\Pi$, $v' = 0$) molecules excited by absorption of the $(A\,^1\Pi, v' = 0 \rightarrow X\,^1\Sigma^+, v'' = 0)$ molecular resonance band, additives up to pressures of several hundred torr had no major effect on the overall absorption in the fluorescence cell. This was demonstrated by the good agreement of quenching efficiencies obtained from Stern-Volmer plots with those deduced from measurements of the pressure dependence of the relative populations in the levels $v' = 0$ and $v' = 1$ when $v' = 1$ was excited [7].
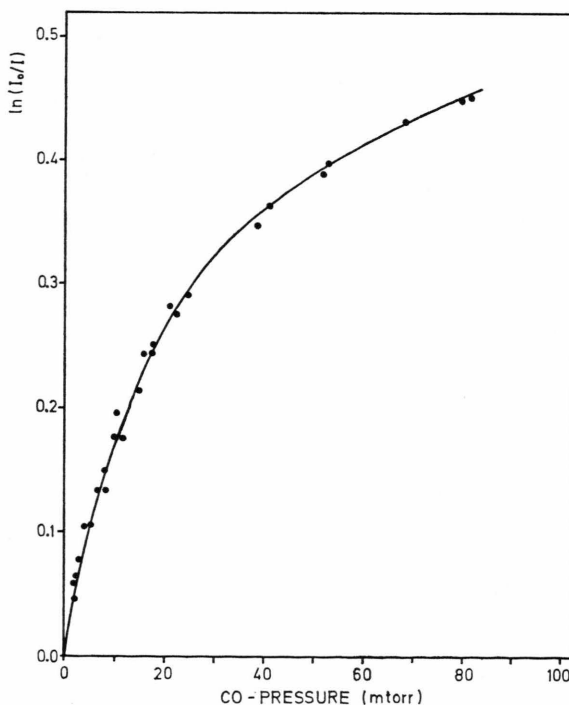

Fig. 2. Absorption of the 1150 Å (B $\rightarrow$ X) sequence by CO.

To investigate the influence of foreign gases on the total absorption of CO, several series of absorption measurements on pure CO and on CO/rare gas mixtures were carried out. For these experiments an absorption cell of 12 cm length was placed behind the exit slit of the monochromator. The transmitted 1150 Å radiation was measured by a photomultiplier coated with sodium salicylate. Figure 2 shows a plot of $\ln(I_0/I)$ vs. CO pressure. The slope of the curve at low CO pressure yields an effective absorption coefficient of $k = 1.5 \times 10^3 \mathrm{cm}^{-1} \mathrm{atm}^{-1}$. In this experiment the pressure in the microwave lamp was 200 mtorr as usual.

Measurements on a 1 : 100 CO/Ar mixture showed — within the error limits — the same dependence of $\ln(I_0/I)$ on CO partial pressure as Figure 2. In addition, experiments were performed in which the change in overall absorption was studied when Ar, He, and Ne up to pressures of several hundred torr were added to CO at varying initial pressures. Up to CO pressures of 50 mtorr no change of the initial absorption could be detected, the error limit being less than $\pm 5\%$ at pressures above 5 mtorr. However, the results of the quenching measurements, reported later, showed that at very low CO pressures the absorption obviously is lowered by the addition of gases like He and Ne. At CO pressures between 50 and 100 mtorr the total absorption was found to increase at the addition of foreign gases. The effect gradually increased both with CO and foreign gas pressure up to maximum values of about 30% at 1 atm total pressure. This showed that the Stern-Volmer plots could not be expected to yield reliable results at CO pressures much higher than 50 mtorr.

Initial quenching measurements showed that the added gases He, Ne, Ar, H_2, and D_2 could be divided into two groups corresponding to high and low quenching efficiencies. Ar, H_2, and D_2 were found to quench the excited CO molecules with nearly unit collision efficiency. Foreign gas pressures not higher than 15 torr were needed to measure the Stern-Volmer lines. Figure 3 shows Stern-Volmer plots for CO pressures ranging from 0.7 to 56 mtorr with argon as quenching gas. The curves can be analysed in terms of the equation

$$I_0/I = 1 + k_M^q \, \tau_{\mathrm{eff}}(M) \tag{1}$$

with k_M^q being the rate constant of the collisional deactivation process, and τ_{eff} the effective radiative

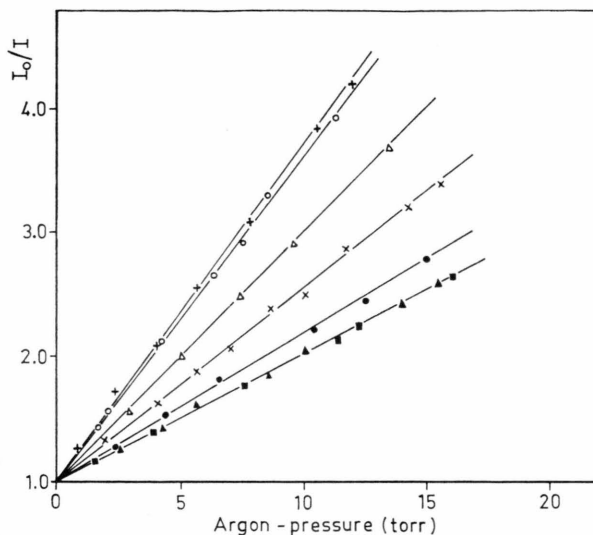

Fig. 3. Stern-Volmer plots of the $(B \to A)$ fluorescence as a function of Ar pressure for different CO pressures; ▲ $p_{CO} = 0.7$ mtorr, ■ $p_{CO} = 1.1$ mtorr, ● $p_{CO} = 4.8$ mtorr, $\times$ $p_{CO} = 12$ mtorr, △ $p_{CO} = 24$ mtorr, ○ $p_{CO} = 38$ mtorr, $+$ $p_{CO} = 56$ mtorr.

lifetime of the excited molecules. In this equation self-quenching of $CO(B, v' = 0)$ in collisions with ground state CO molecules is neglected. From the measurements of Moore and Robinson [11] the rate constant for self-quenching can be estimated to be lower than $1 \times 10^{-9} \mathrm{cm}^3$ molecule^{-1} sec^{-1}. Thus, with effective radiative deactivation probabilities between 1.1×10^7 and $4.5 \times 10^7 \mathrm{sec}^{-1}$ (see below), the above approximation is certainly justified at CO pressures below 10 mtorr ($\hat{=} 3.2 \times 10^{14}$ molecules cm^{-3}). At the highest CO pressures applied, self-quenching could contribute to a maximum of 10% to the total deactivation rate at zero added gas pressure.

As k_{Ar}^q is a constant under all conditions the variation of the slopes of the curves shown in Fig. 3 reflects the veriation of τ_{eff} as a function of CO pressure. The slopes were found to converge in the low and high pressure regions. In these two limiting cases the radiative lifetime is determined either by the radiation of the free molecules consisting of both the $(B \to A)$ and the $(B \to X)$ transitions or by the $(B \to A)$ transition only when the $(B \to X)$ radiation is trapped by resonance absorption. The variation of the slopes of the Stern-Volmer plots as a function of CO pressure is shown in Figure 4. From the limiting value of $\tilde{k}_{Ar}^q$ at low CO pressure, $\tilde{k}_{Ar}^q = 0.10 \pm 0.01$, together with the natural life-

M	$\tilde{k}_M^{\,q}$ (torr^{-1})	$10^{12} \times k_M^{\,q}$ (cm^3 molecule^{-1} sec^{-1})	$\sigma_{\text{eff}}^{\,q}$ (Å^2)	$P_M^{\,q}$ (B$^1\Sigma^+$)	$P_M^{\,q}$ (A$^1 \varPi$)	Table 1. Results of quenching measurements. $P_M^{\,q}$: Quenching probability.
He	0.0022 ± 0.0008	3.1	0.23	0.0074	0.0011	
Ne	0.0025 ± 0.001	3.5	0.48	0.015	0.0043	
Ar	$0.10 \quad \pm 0.01$	139	22.4	0.55	0.08	
H$_2$	$0.14 \quad \pm 0.01$	195	10.7	0.32	0.59	
D$_2$	$0.11 \quad \pm 0.01$	153	11.4	0.34	0.83	

time, $\tau = 22$ nsec, one obtains a rate constant and an effective collision cross section of

$k_{\text{Ar}}^{\,q} = (1.39 \pm 0.14) \times 10^{-10}$ cm^3 molecule^{-1} sec^{-1},
$\sigma_{\text{eff}}^{\text{Ar}} = 22.4 \pm 2.2$ Å^2

for the quenching of CO$(B\,^1\Sigma^+, v' = 0)$ molecules by argon. Also with hydrogen and deuterium as quenching gases the Stern-Volmer plots yielded straight lines for all CO pressures. The results of the quenching measurements with H$_2$ and D$_2$ were curves quite similar to the one in Fig. 4 for argon. Both additives lead to curves with horizontal parts in the low $(1-5$ mtorr) and in the high $(>50$ mtorr) pressure regions. The quenching rate constants calculated from the slopes at low CO pressure are given in Tab. 1 together with the data for the other gases.

Helium and neon were found to be much less effective in quenching the excited CO$(B, v' = 0)$ molecules. Pressures of several hundred torr had to be applied for measuring Stern-Volmer lines. This has remarkable consequences on the observed pressure dependence of I_0/I as is seen from Figure 5. The experimental data points no longer follow a straight line as should be expected, but instead the curve is bended upwards. Such behaviour was measured in the region of CO pressures below 10 mtorr in both cases when Ne or He were used as quenching gases. The lower the CO pressure in these experiments the stronger was the bending of the curves. But these curves always approached asymptotically the dashed line which represents the slope of the curves at vanishing pressure of the foreign gas. At elevated CO pressures $(p_{\text{CO}} > 10$ mtorr) the results for the two gases showed a slightly different behaviour as Ne exhibited no observable deviation of the corresponding slopes of the Stern-Volmer lines from that of the dashed line whereas in the case of helium an increase of the slopes up to 50% was measured in going from the lowest to the highest CO pressures applied. The data given in Tab. 1 were taken from the slopes of the Stern-Volmer curves at

vanishing additive pressure obtained in the experiments with CO pressures below 5 mtorr.

The quenching rate constants were used to obtain effective collision cross sections as usual by dividing $k_M^{\,q}$ by the relative velocity $\bar{c} = (8\,kT/\pi\,\mu)^{1/2}$ of the molecules. The molecular diameters tabulated in Ref. 15 were used to calculate the gas kinetic cross sections σ_{gk} and the quenching efficiencies $P_M^{\,q} = \sigma_{\text{eff}}/\sigma_{\text{gk}}$. The results are collected in Table 1.

Discussion

A stringent premise for the determination of quenching efficiencies from measurements of relative fluorescence intensities as a function of added gas pressure is that 1. the amount of excited molecules produced in the primary excitation process, and 2. their effective radiative lifetime and quenching cross sections remain constant throughout the experiment.

1. When resonance absorption is used for excitation, the most serious problem usually is the change of primary absorption due to pressure broadening of the absorption lines which affects the production rate of excited molecules. As can be seen from the experimental results reported in Ref. 16, pressure broadening usually has a strong influence on the line profile of absorption lines at pressures above 10 torr. Since the oscillator strength keeps constant, the increase in line width results in a rapid decrease in maximum absorption. If for instance the half width due to pressure broadening is twice as large as the Doppler width, the maximum absorption coefficient is decreased to about 1/4 of its original value in the center of the Doppler line profile.

The effect of pressure broadening on the primary absorption will be most pronounced in cases in which the overlap of the emission and the absorption lines is poor at low pressure. In this case a broadening of the absorption line will cause an increase of the total absorption with pressure, since with increasing pressure the absorpiton is facilitated

at those wavelengths at which the emission line is strongest. This obviously is the reason for the large effects of pressure broadening on the absorption which were observed in previous work when atomic lines were used for excitation which were not exactly in resonance with the molecular absorption lines [2, 4]. The much weaker effect of pressure broadening on the overall absorption observed in the present work then must be explained by the exact matching of the emission and the absorption lines when molecular resonance bands are used for excitation. The absorption curve shown in Fig. 2 can be understood in terms of Doppler and Lorentz broadened lines emitted by the hot gas in the microwave discharge which are absorbed by the gas in the fluorescence cell at room temperature exhibiting narrow Doppler shaped absorption lines. The emission lines might be self-reversed to some extent. As is seen from Fig. 2, at low CO pressures the absorption follows Beer's law. However, at higher CO pressure the centers of the absorption lines will show total absorption. Further absorption can only occur on the wings of the absorption lines resulting in lower effective absorption coefficients. This explains the inclination of the curve shown in Figure 2.

Those quenching measurements in which the maximum pressures of the added gas were less than 15 torr obviously were not affected by pressure broadening. This can be concluded from the fact that for Ar, H_2, and D_2 the Stern-Volmer plots showed straight lines under all conditions. However, when pressures of several hundred torr were needed, as was necessary in the measurements with He and Ne, effects of pressure broadening of the CO absorption lines are clearly demonstrated by the results. At low CO pressure the reduction in maximum absorption due to pressure broadening by He and Ne is not compensated by the additional absorption on the wings of the broadened lines as the intensity of the emission lines in these regions is lower than in the center of the lines. The result is a decrease of the net production of excited molecules in the field of view of the photomultiplier. This explains the deviation of the measured I_0/I values from a straight line towards higher values, which was observed in the Stern-Volmer plots for He and Ne at low CO pressure (Figure 5).

2. The $(B\,{}^1\Sigma^+ \to X\,{}^1\Sigma^+)$ system of CO is one of the few molecular band systems in which a strong effect of resonance trapping on the effective lifetime

of the excited state has been observed [11]. The lifetime τ_{eff} of the $B\,{}^1\Sigma^+$, $v' = 0$ molecules is determined by the sum of probabilities of all radiative and collisional processes depopulating this state

$$1/\tau_{\text{eff}} = \sum_{v''} A_{(B,\,v'=0 \to A,\,v'')} + \sum_{v''>0} A_{(B,\,v'=0 \to X,\,v'')}$$
$$+ g\,A_{(B,\,v'=0 \to X,\,v''=0)} + \sum_M k_M^q(M) \qquad (2)$$

where $A_{(U \to L)}$ are the Einstein transition probabilities for radiation from the upper state U to lower
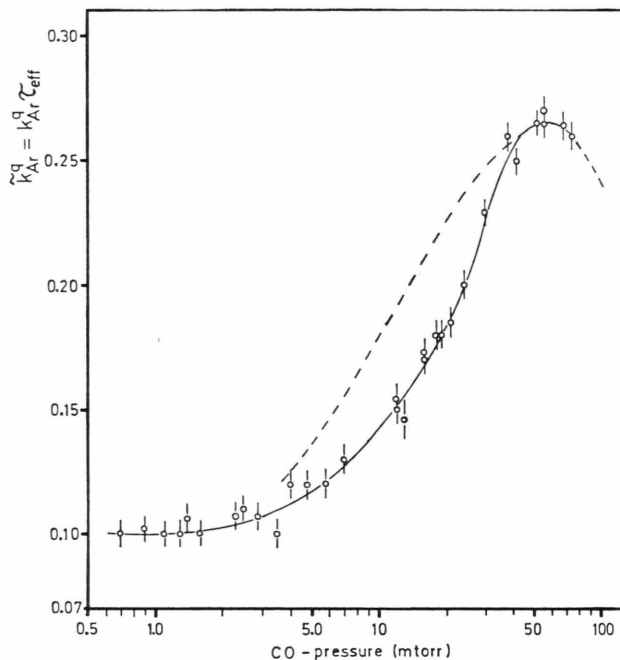

Fig. 4. Slopes of the Stern-Volmer plots for Ar as a function of CO pressure; dashed line: results of Ref. 11.
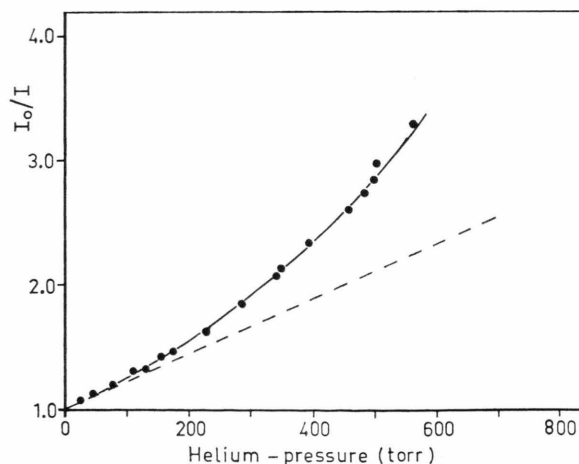

Fig. 5. Stern-Volmer plot of the $(B \to A)$ fluorescence intensity as a function of He pressure at a CO pressure of 1.3 mtorr.

states L, and $k_M{}^q$ are the quenching rate constants of species M. The so-called "trapping factor" g is a measure to which extent resonance trapping of the ($B, v' = 0 \rightarrow X, v'' = 0$) band occurs. It varies between one at low CO pressure and zero at high CO pressure where the resonance radiation is totally imprisoned [17].

The results of the quenching measurements with Ar, H_2, and D_2 (Fig. 4) show that in these experiments resonance trapping of the vacuum-u. v. fluorescence becomes noticable at pressures above 4 mtorr. The dashed curve in Fig. 4 shows the results of Moore and Robinson [11] on the pressure dependence of the effective lifetime of the $B, v' = 0$ state. The two curves in Fig. 4 are normalized at 60 mtorr. It is seen that in both experiments the pressure effect occurs in nearly the same pressure range. It should be stated that due to the different geometries of the fluorescence cells the curves need not be identical. Whereas Moore and Robinson could not extend their lifetime measurements to such low CO pressures where τ_{eff} becomes equal to the natural lifetime and independent on CO pressure, this pressure region was clearly reached in our experiments. This is an important pre-condition for the interpretation of the measurements because absolute values of the lifetime have to be known in order to calculate quenching rate constants from the slopes of the Stern-Volmer lines. The natural lifetime of the $CO(B, v' = 0)$ state has been measured repeatedly, and the reported data are in good agreement [12, 13]. For the analysis of our results we used the most recent value of $\tau = 21.8 \pm 0.3$ nsec given by Imhof and Read [12].

In the quenching measurements with Ar, H_2, and D_2 discussed above, the effective radiative lifetime was found to be dependent on the CO pressure but was constant in the course of each experimental run. This is no longer true in part of the experiments with He and Ne. The reason is that pressure broadening of the CO absorption lines has a strong influence on the degree of resonance trapping. As the absorption coefficients at the centers of the absorption lines are strongly decreased at higher pressures of added gases, the extent of resonance trapping and with it the effective radiative lifetime are decreased likewise. Therefore, when operating with He and Ne at CO pressures above 4 mtorr where the initial steady state intensity I_0 is influenced by resonance trapping, pressure broadening will gradually

reduce the extent of resonance trapping and τ_{eff} will not be constant throughout an experimental run. The intensity I then no longer follows the simple Equation (1). In addition, this variation of the absorption properties caused by the added gas may change the geometry factor which enters into the intensity of the fluorescence radiation.

An opposite effect on the extent of resonance trapping as the pressure is increased might result from rotational relaxation. The primary rotational distribution in the $B^1\Sigma^+$, $v' = 0$ state resulting from the absorption of the resonance band, probably is nonthermal or corresponds to a temperature above room temperature. At the addition of foreign gases up to high pressures as in the experiments with He and Ne, this distribution will gradually be shifted to a room temperature distribution by rotational relaxation processes. As the rotational constant of the B state is very close to that of the ground state, the fluorescence from the relaxed rotational distribution will meet a higher mean population in the rotational levels of the ground state than did the fluorescence from the primary distribution. As a consequence, the mean absorption coefficient and with it the extent of resonance trapping will increase. In addition, changes of the rotational distribution of the excited molecules could lead to changes of the quenching efficiency if the cross section is strongly dependent on the rotational quantum number.

In the range of medium and high CO pressures, the different effects of rotational relaxation and pressure broadening of the absorption lines on the production rate and the effective radiative lifetime of the excited molecules, and on the geometry of the fluorescing medium, which have been discussed above, obviously will influence the fluorescence intensities in those quenching experiments where He and Ne up to several hundred torr are added to the CO. Although under these conditions the plots of I_0/I vs. pressure showed straight lines, these lines cannot be analysed in terms of the simple Stern-Volmer Equation (1). Therefore, we have used only those results from the He and Ne experiments which were obtained at CO pressures below 4 microns where the trapping of resonance radiation is negligible. The effect of rotational relaxation on the quenching efficiency is expected to be of minor importance in this case.

As concluded in 1. and 2. our results at CO pressures above 50 mtorr are less reliable than those at

lower CO pressures, due to the changes of the primary absorption at the addition of foreign gases which was observed in the absorption measurements. However, from our measurements on Ar, H_2, and D_2 it is still obvious that the slopes of the Stern-Volmer lines become nearly independent on CO pressure above 50 mtorr (Figure 4). The ratio of the effective lifetime in the high and low pressure regions is found to be 2.7. Taking the natural lifetime to be 22 nsec [13] the effective lifetime at 60 mtorr is calculated to be 59 nsec, which is in fair agreement with the value of 71 nsec measured by Moore and Robinson [11]. Therefore, our results support the value of the transition probability of the $(B \rightarrow A)$ transition, $A_{(B \rightarrow A)} = 1.11 \times 10^7 \, \text{sec}^{-1}$, which these authors derived from their measurements.

The results presented in Table I for the collissional quenching of the $B\,^1\Sigma^+$, $v'=0$ excitation of CO molecules prove He and Ne to be less effective than Ar, H_2, and D_2, whose cross sections are nearly gas kinetic. Argon is even more effective than the molecular gases hydrogen and deuterium. If, however, one compares these results with the recently determined quenching probabilities of the $A\,^1\Pi$, $v'=0$ excitation of CO there is some similarity for the rare gases He, Ne, and Ar. Their respective probabilities for B state deexcitation are larger by a factor of $3-7$. This supports the assumption that in both cases quenching occurs mainly by collision induced transitions into nearby electronically excited states, whereas transfer of the total energy into vibration of the ground state and into translation is of minor importance.

In the case of the $B\,^1\Sigma^+$, $v'=0$ state the spin allowed transition to the $A\,^1\Pi$ and $I\,^1\Sigma^-$ state should be favoured. However, in addition to the lower lying a, a', d, and e states two more triplet states, f and b, are accessible, too. Due to this enlarged number of possible deactivation channels for CO $(B\,^1\Sigma^+)$ as compared to CO $(A\,^1\Pi)$ one should expect the respective quenching probabilities to increase.

The occurance of spin-forbidden processes in collissions of small molecules like N_2, NO, and CO is still questionable [18]. We believe that the large quenching cross sections observed for the CO $(A\,^1\Pi)$ and CO $(B\,^1\Sigma^+)$ states cannot be explained without the assumption of such processes. Further evidence for this assumption is obtained from recent quenching experiments with vibrational excited CO $(A\,^1\Pi)$ [8]. A search for product states could clarify this point.

The large cross section of argon as compared to helium and neon points to the possibility that in this case a collision complex is formed which might survive several vibrations. Such a complex formation would greatly enhance the quenching efficiency. Dissociative collisions are not expected to occur in the discussed processes although a weak predissociation was observed for $B\,^1\Sigma^+$, $v'=0$, $J=38$.

H_2 and D_2 were found to quench CO $(B\,^1\Sigma^+$, $v'=0)$ with nearly equal collision efficiency which, however, is about a factor of 50 larger than that of He. Compared to $A\,^1\Pi$, $v'=0$, the $B\,^1\Sigma^+$, $v'=0$ state is quenched with slightly lower cross sections by hydrogen molecules. These results suggest that with H_2 and D_2 the quenching collisions are reactive, resulting in a dissociation of the hydrogen molecules or in formation of radicals like CH, OH, or HCO. Therefore, attempts could be made to observe such reaction products.

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