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Elusive $C\ ^3\Pi_u$ state lifetime of molecular nitrogen

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The N_2 *C*-state lifetime is crucial, for instance, in understanding the action of the nitrogen laser. Although it has been extensively studied in a great number of experiments, the results do not converge and they scatter much more than the individually quoted errors. Thus, a recent measurement with a given error of 1% yields a result which is a 24% higher value than the earlier accepted average value. The present experiments suggest that the scattering among the results is due to a unique systematic error originating from a joint action of resonance trapping and collisional transfer. The recommended weighted average value is $\tau(N_2, C,\ v=0)=37.4\pm1.0$ ns.

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The radiative lifetimes of the *A*, *B*, and *C* states of molecular nitrogen are crucial in understanding the laser action of the $C\rightarrow B$ and $B\rightarrow A$ emission, and the condition $\tau_c \ll \tau_B \ll \tau_A$ is essential for creating the inversion in both the systems. Since the $C\rightarrow B$ emission (the second positive system) is very strong in the visible region, the *C*-state lifetime has been studied by a great number of investigators using various techniques [1–8]. However, as seen from Fig. 1, the results do not converge and they scatter much more than the individually quoted errors. In particular, the most recent measurements [7,8] using laser-induced fluorescence yield considerably longer lifetimes than the commonly accepted value $[\tau_C(v=0)\approx 37$ ns]. Accordingly we have repeated the lifetime measurements of the *C-B* (0,0) band using the high-frequency deflection technique [9], which has earlier been applied for detailed lifetime investigations of individual rotational levels of the N_2 *C* state [5]. In the present experiments a 20-mA beam of 20-keV electrons was swept at 460-kHz frequency in front of a slit of a gas cell containing nitrogen gas at 1–110 mTorr pressure.

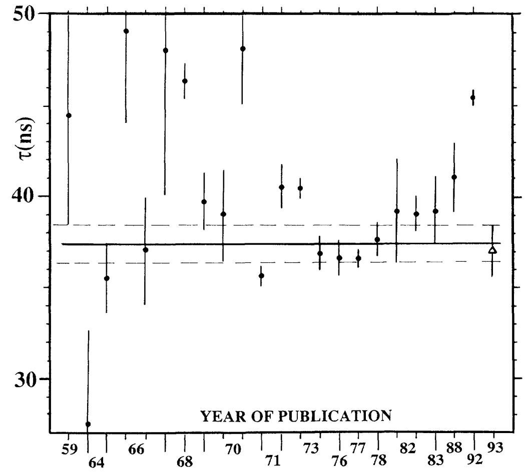

FIG. 1. Published experimental values of the lifetime τ of the $C\ (v=0)$ state in molecular nitrogen. The results prior to 1977 are discussed in the review [1] while the later "year of publication" refers to the following references: 77, [2]; 78, [3]; 82, [4,5]; 83, [6]; 88, [7]; 92,[8]; 93, present work.

The results for the (0,0) band are shown in Figs. 2 and 3. At 1 mTorr the decay curve is strongly distorted and nonexponential, and contains very long-lived components; but with increasing target pressure the decay curve gradually restores itself to a "normal" shape, and for $p>50$ mTorr the pressure dependence (Fig. 3) follows the expected linear (Stern-Volmer) behavior with a slope corresponding to what has been observed by earlier investigators (about $10^4\ \mathrm{s}^{-1}\,\mathrm{mTorr}^{-1}$, cf. Ref. [10]). Similar dependences at low pressures are also found for the (1,2) and (2,1) bands.

The observed pressure dependence (Fig. 3) (see also Ref. [11]) is remarkable and demands an explanation. Also other investigators have noted deviations from a single exponential (cf. Ref. [12]), while this has escaped the attention in most of the published studies. Thus there are

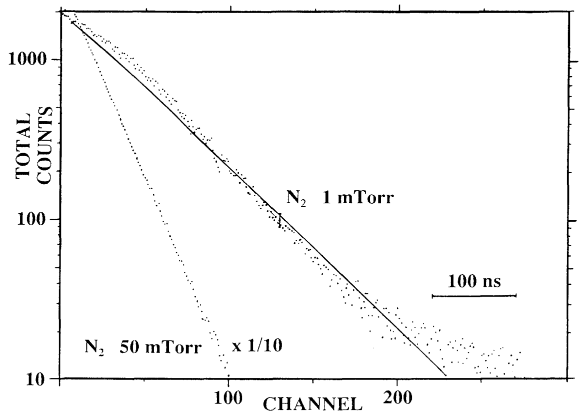

FIG. 2. Decay curves of the (0,0) band of the N_2 *C-B* transition measured at two different N_2 target pressures using the high-frequency defection technique using a 20-mA excitation current. At 50 mTorr pressure the decay curve is a single exponential yielding a "normal" value $\tau=36.7$ ns. At 1 mTorr the decay curve is strongly distorted and is no longer a single exponential having a slope roughly corresponding to $\tau\sim84$ ns in its middle part. The continuous line is a plot of Eq. (9) with $ai[X]=0.6$, $k_{BY}[M]=0$, and the known decay constants A_B and A_C.

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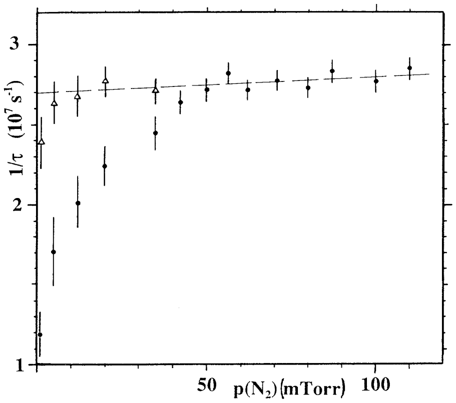

FIG. 3. Inverted lifetimes of the C ($v=0$) state in N_2 measured at various pressures p of the N_2 target gas (dots). From 50–110 mTorr the behavior follows what is expected from collisional quenching (a Stern-Volmer behavior), while $1/\tau$ gradually drops for $p<50$ mTorr. The addition of 50 mTorr krypton (triangles) essentially eliminates this anomalous behavior at lower pressures.

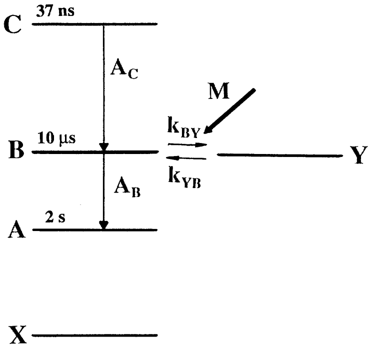

FIG. 4. Suggested processes in the decay of the N_2 C state which lead to the anomalous pressure dependence displayed in Fig. 3. Since the B state is long-lived (~ 10 μs), concentrations $[B]$ are built up after the excitation pulse which are high enough to cause a considerable resonance trapping of the C-B emission. However, there are a number of other states Y (particularly belonging to the A state and the W state) which are so close lying to B that a considerable transfer may take place from B to Y immediately after the excitation. This transfer will diminish $[B]$, thus reducing the trapping of the C-B emission with increasing target pressure.

reasons to believe that we are facing a kind of systematic error that strongly depends on the experimental conditions and not on a "universal" systematic error such as cascades or collisional quenching. Such an error is radiation trapping, which has been considered for many years in the case of resonance transitions. However, as demonstrated in our laboratory [13–15], also trapping of nonresonance transitions may cause considerable distortions in lifetime measurements, provided that the lifetime of the lower state is long enough and the excitation efficiency is high. These conditions are present in the present case (Fig. 4), since the lifetime (~ 10 μs) of the B state is long enough to allow concentrations to be built up which are large enough to cause trapping of the $C\rightarrow B$ emission and a lengthening of the observed lifetime. However, the trapping must then increase with increasing target pressure, but actually we observe a *decrease* with pressure. Therefore we have to consider an additional process that will decrease the B state population with increasing target pressure. Collisional transfer from the B state to another neighboring state Y would be such a process. Actually collisional transfer processes in N_2 involving the B state have been known for a long time (cf. Ref. [16], and references given therein). Concerning the lowest ($v=0$–2) levels of the B state, the $W\,^3\Delta_u$ levels ($v=0$–2) are close in energy [$W(v=0)$ as close as 70 cm^{-1} to $B(v=0)$] and the $A\,^3\Sigma_u^+$ levels ($v=7$–10) are also close lying (of the order of $\Delta E\sim kT=200$ cm^{-1} at room temperature). However, since the transfer rate between two levels B and Y is only smoothly dependent on their energy difference [cf. Eq. (3)] and there is a great amount of Y levels disposable, no drastic differences in the total transfer from the lowest ($v=0$–2) B levels are expected.

Thus we propose that the observed pressure dependence of τ_C is due to radiation trapping of the C-B emission, and the trapping will decrease with increasing pressure thanks to fast removal of the B-state population by collisional transfer to other N_2 levels. To test this proposal further, we will deduce an expression for the expected C-state decay curve influenced by the suggested processes. For this purpose we will make a number of simplifying assumptions. We restrict the discussion to the rotationless $v=0$ levels of the C and B states and neglect the branchings of the C ($v=0$) decay, letting $A_C(=1/\tau_C)$ and $A_B(=1/\tau_B)$ denote the total transition probabilities. This simplification is justified in view of the discussion above and the fact that the Franck-Condon factors for the C-B $(0,v'')$ bands are 0.40, 0.33, and 0.16 for $v''=0,1,2$, respectively. If B mainly communicates with one close-lying level Y, the rate equations for the mutual transfer $B\rightleftarrows Y$ are

$$d[B]/dt=-A_B[B]-k_{BY}[B][M]+k_{YB}[Y][M]\ , \tag{1}$$

$$d[Y]/dt=-k_{YB}[Y][M]+k_{BY}[B][M]\ , \tag{2}$$

where $[M]$ is the concentration of the colliding species M. The possible radiative decay of Y is neglected and the rate coefficients k_{BY} and k_{YB} are related by detailed balance through the relation

$$k_{YB}=gk_{BY}\exp(-\Delta E_{BY}/kT)\ , \tag{3}$$

where g is a statistical factor. If we further assume that the initial population $[Y]_0$ is small and consider a time interval when the decay of $[B]$ proceeds faster than the feeding of B from radiative decay from C and reverse transfer from Y, the solution to (1) is

$$[B]=[B]_0\exp\{-(k_{BY}[M]+A_B)t\}\ . \tag{4}$$

This population $[B]$ reduces the transition probability A_C to the experimentally measured value A_C^{expt} because of resonance trapping. If the trapping is assumed to take place within an infinite cylinder with radius R, we may write [17]

$$A_C^{\rm expt}=A_C(1-k^0R\pi/2\sqrt{2})\ , \tag{5}$$

where k^0 is the absorption coefficient at the center of the absorbed transition, which is given by

$$k^0=(\lambda_{CB})^3A_C[B]/v_B8\pi^{3/2}\ . \tag{6}$$

Here λ_{CB} is the wavelength of the $C\rightarrow B$ emission and v_B the velocity of the N_2 molecules in the B state, while the ratio of the statistical factors $g_C/g_B=1$ and has been omitted in Eq. (6). The B-state population is built up both via direct excitation from the ground state as well as via the C state and we may write

$$[B]_0\propto i\Gamma(\tau_B+\tau_C)[X]\ , \tag{7}$$

where i is the exciting current, Γ the pulse length, τ_B and τ_C the electron excitation cross sections, and $[X]$ the ground-state population. We may estimate the expected magnitude of $[B]$ which is required to cause the observed increase in τ for instance from 37 to 84 ns and 1 mTorr by resonance trapping in the following way. Neglecting the variation of λ_{CB} within the $(0,v'')$ bands, we find from Eq. (5) that the observed lifetime lengthening corresponds to $k^0=0.03$, assuming $R=10$ cm. Introduced into Eq. (6) with $v_B=500$ m/s this gives $[B]=4.6\times10^{10}$ cm$^{-3}=10^{-3}[X]$. It seems very probable that such high-B-state populations may be built up using the present powerful excitation if the depopulation predominantly proceeds via the slow $B\rightarrow A$ radiative decay.

From (4)–(7) we get the time-dependent transition probability

$$A_C^{\rm expt}(t)=[1-ai[X]\exp\{-(k_{BY}[M]+A_B)t\}]A_C\ , \tag{8}$$

where the factor a contains λ_{CB}, v_B, A_C, Γ, and $\tau_{B,C}$, i.e., it remains constant during the experiments. The experimentally measured (nonexponential) fluorescence decay rate of the C state will then be

$$I_C(t)=-d[C]/dt=A_C^{\rm expt}(t)[C]\ . \tag{9}$$

Inserting (8) into (9) and integration gives

$$[C]=[C]_0\exp\{-A_C(t-ai[X](1-\exp\{-(k_{BY}[M]+A_B)t\})/(k_{BY}[M]+A_B))\}\ . \tag{10}$$

With (8) and (10) inserted into (9), we may calculate the expected C-state decay curve influenced by the joint action of trapping and transfer processes for various values of i, $[X]$, and $[M]$.

A reasonable fit to the measured decay curve at 1 mTorr N_2 is obtained by intensity normalization at $t=0$ and by putting $ai[X]=0.6$ and $k_{BY}[M]=0$ into Eq. (9) (Fig. 2). As a first test of Eq. (9) we will keep $[X]$ (i.e., the N_2 target pressure) constant at 1 mTorr and add 15 and 50 mTorr Kr. As seen from Fig. 5 this catalyzer causes a shortening of τ_C, and at $[M]=[\mathrm{Kr}]=50$ mTorr, τ is about 42 ns approaching its "normal" value. For larger t values the measured curves are roughly reproduced by Eq. (9) if we put $k_{BY}=4\times10^{-9}$ cm^3 s^{-1}. This might be compared to the estimated rate coefficients for transfers to upper B-state levels, which are of the order $k\sim10^{-10}$ cm^3 s^{-1} [18]. In other molecules, for instance in the case of transfer to the A state in CO, rate coefficients as large as 4×10^{-8} cm^3 s^{-1} [19] have been found. The measurements were repeated at higher N_2 pressures with added 50-mTorr Kr, and the results are displayed as triangles in Fig. 3. As seen from Fig. 3 the addition of Kr almost restores the pressure dependence to the expected Stern-Volmer behavior.

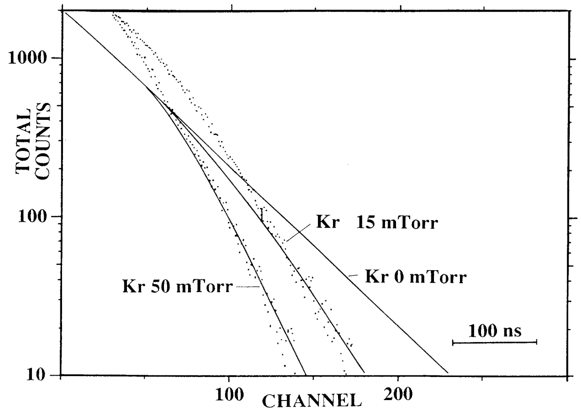

FIG. 5. Decay curves of the (0,0) band of the N_2 C-B transition measured at 1 mTorr N_2 target pressure with added krypton gas at 15 and 50 mTorr, respectively. The continuous lines are plots of Eq. (7) with $k_{BY}=4\times10^{-9}$ cm^3 s^{-1}. Thus the addition of a second catalyzer gas (M) gradually restores τ to its normal value in accordance with the processes suggested in Fig. 4 and described by Eq. (9).

The conditions are more complicated when only N_2 is used as a target gas, i.e., when $[M]=[X]$. The transfer certainly increases with increasing $[X]$ but the faster depopulation of the B state is then partially counterbalanced by a larger initial population $[B]_0$. However, since $[B]_0$ increases linearly with $[X]$ [Eq. (7)] while $k_{BY}[X]$ enters in the exponent in Eq. (4), the latter term will dominate with increasing time and hence the trapping effects will be larger at low N_2 target pressures. An alternative way of testing Eq. (9) in the case of a pure N_2 target is to keep the pressure constant and vary the exciting current (or the pulse length). A reduction of the exciting current i would then reduce $[B]$, independent of subsequent transfer processes. Figure 6 shows two decay curves at 1 mTorr N_2 pressure where the original 20-mA current has been reduced to 13 and 7 mA, respectively. As expected the deduced lifetimes become gradually shorter and are well represented by Eq. (9) with $ai[X]=0.6\times\frac{13}{20}$ and $0.6\times\frac{7}{20}$, respectively.

The very long-lived component observed in Fig. 2 and by other investigators is not reproduced by Eq. (9) and has probably another origin, namely a collisional transfer from the metastable $E\,^3\Sigma_g^+$ state to the C state (cf. Ref. [20]).

It is of interest to consider the possible influence of the predicted $B\rightarrow Y$ transfer upon measured B-state lifetimes. At some time after the excitation an equilibrium is achieved where $[B]$ and $[Y]$ are determined as fractional populations f_B and f_Y (given by the Boltzmann equation) of the total population $[B]+[Y]$, i.e.,

$$[B]=f_B([B]+[Y]) \ , \tag{11}$$

$$[Y]=f_Y([B]+[Y]) \ . \tag{12}$$

If (11) and (12) are introduced into the sum of Eqs. (1) and (2) we get

$$\begin{aligned}\frac{d[B]}{dt}+\frac{d[Y]}{dt}&=d\frac{([B]+[Y])}{dt}\\&=-A_Bf_B([B]+[Y])\end{aligned} \tag{13}$$

or

$$\frac{d[B]}{dt}=-A_Bf_B[B] \ .$$

In other words, when equilibrium is achieved, the total population as well as $[B]$ will decay with the same constant $=A_Bf_B$. Since $f_B=\frac{2}{3}$ or $\frac{1}{2}$, depending on the statistical factor of the Y state, this means that the transfer $B\rightleftarrows Y$ would lengthen τ_B by a factor of $\frac{3}{2}$ or 2 at equilibrium. However, in practice, a number of N_2 levels are involved in the transfer process, starting from the fast removal of a given B level, and this would counterbalance this lifetime lengthening effect. It would be interesting to introduce these processes into the discussion concerning the nitrogen laser action.

In summary we suggest that the scattered results of the earlier investigation of the N_2 C-state lifetime are consequences of a unique combination of systematic errors following radiation trapping of the $C\rightarrow B$ emission which disappears at higher target pressures where the B population is removed by fast collisional transfer to other close-lying N_2 levels (presumably belonging to the A and/or the W state). Thus a lifetime lengthening occurs which is particularly pronounced in experiments at low pressures using high excitation efficiencies such as the recent laser-included fluorescence experiments [8]. If the present measurements are extrapolated to zero pressure following the Stern-Volmer plot (dashed line in Fig. 3) the result is $\tau_C(v=0)=37.0\pm1.5$ ns. The same result is obtained from repeated measurements at low excitation current. We may also give a "recommended" value of $\tau_C(v=0)$ based upon all existing data where the presently discussed systematic errors are taken into account. If "high" values are given low weight factors, our recommended weighted average value is

$$\tau_C(v=0)=37.4\pm1.0 \text{ ns} \ .$$

Although the present investigation has not proved that this is the "true" value of $\tau_C(v=0)$, it should have a higher confidence level than an unweighted average value of earlier investigations, several of which must have been influenced by the presently discovered systematic errors. Moreover, the recommended value is in fair agreement with *ab initio* calculations (cf. Ref. [21]), which yield $\tau=36.7$ ns.

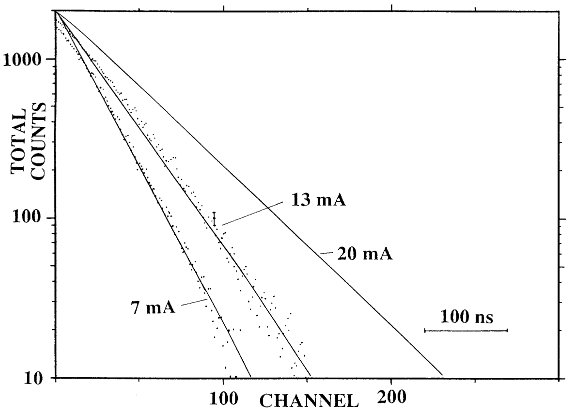

FIG. 6. Decay curves of the (0,0) band of the N_2 C-B transition measured at 1 mTorr N_2 target pressure with the excitation current reduced from the original 20 mA to 13 mA and 7 mA, respectively. The continuous lines are plots of Eq. (9) where the 20-mA curve is identical to the curve in Fig. 2 (i.e., the fit using $ai[X]=0.6$), and the 13- and 7-mA curves are plotted with $ai[X]=0.6\times\frac{13}{20}$ and $0.6\times\frac{7}{20}$, respectively. Thus the reduction of the excitation current gradually restores τ to its normal value in accordance with the processes suggested in Fig. 4 and Eq. (9).

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