The title of the document is "LONG-LIVED Ka = 0, 2B1 STATES OP N02: A DIRECT MEASUREMENT USING A TUNABLE DYE LASER." The author is Haas, Y., and the publication date is 1975-05-01.
LONG-LIVED Ka = 0, \( ^2B_1 \) STATES OF NO\(_2\):
A DIRECT MEASUREMENT USING A TUNABLE DYE LASER

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May 1975

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

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Long-lived $K_a = 0, {}^2B_1$ States of NO$_2$:  
A Direct Measurement Using a Tunable Dye Laser

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Narrow-band (1 GHz) excitation coupled with selection of specific  
emission bands has been used to measure the lifetimes of some $K_a = 0,  
{}^2B_1$ states of NO$_2$. In contrast with previous experiments and expectations of short lifetimes based on analysis of possible perturbations in the electronic manifold, these states exhibit long collisionless lifetimes of $33 \pm 4 \mu$s. Their quenching cross-sections are found to be larger than gas kinetic, and much larger than that for the unresolved fluorescence.
The interpretation of the visible absorption and emission spectra of NO$_2$ remains a controversial subject, despite the considerable effort spent on its investigation. Both spectra are extremely dense and complex, and only small portions have been analyzed.\textsuperscript{1,2} Neuberger and Duncan\textsuperscript{3} were the first to find that the fluorescence lifetime of NO$_2$ is anomalously long when compared to the lifetime obtained from the integrated absorption coefficient. This effect is believed to arise from interactions between the different electronic levels in the visible region. At least three such levels are involved: the $^2A_1$ ground state and the $^2B_1$ excited state, which correlate with the $^2\Pi_u$ linear configuration, and the $^2B_2$ excited state. Interactions between these states which may lead to a lengthening of the radiative lifetime have been discussed by Douglas,\textsuperscript{4} Gardner and Kasha,\textsuperscript{5} and many others. An analysis of the perturbations involved suggests that excitation of $K_a = 0$ lines of the $^2B_1$ state should produce relatively unperturbed states with shorter lifetimes. Experimental support for this hypothesis was first drawn from the fact that these $K_a = 0$ lines were prominent features in the absorption spectra analyzed by Douglas and Huber.\textsuperscript{1}

Despite much effort\textsuperscript{6,7} to observe short-lived states directly, only two such observations have been reported to date. The first of these involved the above-mentioned $K_a = 0$ lines,\textsuperscript{8} but its accuracy was severely limited by poor signal-to-noise and lack of shot-to-shot stability in the laser
employed. The second of these observations\textsuperscript{9} involved not the $K_a = 0, {^2}B_1$ lines, but rather a $5{^2}B_2$ rotational level pumped by the 488 nm line of an argon ion laser. A lifetime of $3.39 \pm 0.36 \mu s$ was obtained from the linewidth of the microwave-optical double resonance signal.

We wish to report here the direct observation that $K_a = 0, {^2}B_1$ lines near 454.8 nm do not have short lifetimes expected from previous experimental results\textsuperscript{8} and perturbation analysis\textsuperscript{4,5,8}. Two of us\textsuperscript{10} have recently reported the observation of sharp and intense features in the $\Delta v_2 = -1$ NO$_2$ fluorescence upon scanning a tunable dye laser excitation source. For one such feature which occurs near 454.8 nm, there is a one-to-one correspondence between the excitation spectrum and the lines found in absorption.\textsuperscript{1} Also, an analysis of the resolved fluorescence\textsuperscript{10} shows that these lines correspond to perpendicular transitions to states with $K_a = 0$, in agreement with the assignment of Douglas and Huber. Thus, the upper electronic state is $^{2}B_1$.

We have used the same technique of isolating a small part of the fluorescence spectrum to obtain the lifetime. Only in this manner could we be sure that we were measuring the lifetime of the directly populated $K_a = 0$ states.

Extreme care was used to avoid problems arising from laser instability, geometrical effects and sample mishandling. Figure 1 shows the experimental arrangement. A nitrogen-laser-pumped dye laser of 1 GHz bandwith (Moleclectron DL-300 pumped by Moleclectron UV-1000) was used to excite NO$_2$ in a 22-liter
bulb connected to a greaseless vacuum system. Pressures were measured with a capacitance manometer (MKS Baratron, Type 300BH-1 Head). The laser frequency was scanned (Molectron Scanning Unit Model DL-040B), and fluorescence at right angles to the beam was observed by two photomultipliers. One photomultiplier (EMI 9659B, PM-1) was equipped with a blue cutoff filter (Schott RG-530) and observed "red" fluorescence with $\lambda_{\text{fluor}} > 530$ nm. The second photomultiplier (RCA 8575, PM-2) observed fluorescence which was focused using f/10 optics and resolved by a monochromator (Spex, 3/4-m). The monochromator was set to pass "blue" fluorescence 750 cm$^{-1}$ below the excitation line with a bandpass of roughly 90 cm$^{-1}$ (FWHM, 2 mm slits). One problem which may arise when using a monochromator to resolve the fluorescence is that the measured low-pressure lifetime may be shorter than the real lifetime due to the possibility of molecules leaving the field of view of the optics before fluorescing. In order to avoid this problem, the monochromator was positioned so that the image of the fluorescence was at right angles to the 5-cm high slit. For such an arrangement, it is the slit height which determines the maximum lifetime which may be measured. Experiments which will be discussed below indicate that for the blue fluorescence this maximum lifetime is longer than 40 $\mu$sec for the optical arrangement used in these experiments. Since the field of view for PM-1 was much larger, such geometrical effects are negligible for the lifetime determination of the red fluorescence.
A small part of the laser beam was also made to pass through a 1-torr cell of NO$_2$. Fluorescence from this cell was focused into a monochromator (1/4-m, Jarrell Ash with 150 µ slits, 20 Å FWHM) and observed with a third photomultiplier (RCA 8575, PM-3). This monochromator was also set to pass fluorescence 750 cm$^{-1}$ below the laser excitation. The signal from the photomultiplier tube was integrated, averaged and displayed on a chart recorder. The excitation spectrum thus recorded is in excellent agreement with that obtained by Robrish and Rosen. 10b

At specific lines in the excitation spectrum, the laser scan was stopped and the lifetime measurements were made using the 22-liter bulb for both the red and the blue fluorescence. To obtain improved signal-to-noise many fluorescence traces were digitized (Biomation 8100 Transient Recorder) and averaged (Northern 575 Signal Averager). During the period in which the fluorescence was averaged, typically 2-5 min., the laser remained stable in frequency to ~ 1 GHz as judged by the signal intensity of the excitation spectrum.

Fluorescence in either the blue or red region appeared to decay with a single exponential, and linear Stern-Volmer kinetics were obtained over nearly two orders of magnitude in pressure. Reciprocal lifetimes as a function of pressure are shown in Fig. 2 both for the red fluorescence and for the blue fluorescence excited at each of the Q(11) and Q(13) lines.

A number of experiments were performed to ensure that there
were no geometrical effects which might cause shortening of the lifetime and to ensure that the fluorescence observed was from the sharp features of the $\Delta v_2 = -1$ excitation spectrum. Firstly, at 1.3 mtorr of NO$_2$ a lifetime of 18 µsec was measured for the blue fluorescence when excited on the Q(13) line. Without changing the geometry, the monochromator was tuned to observe the fluorescence at 560 nm which yielded a lifetime of 40 µsec. Therefore, the blue fluorescence lifetime was not appreciably shortened by the geometry and was certainly different in temporal behavior from the red fluorescence. Secondly, excitation of 5.4 mtorr of NO$_2$ at the same line gave a lifetime of 8 µsec for the fluorescence centered on the $\Delta v_2 = -1$ feature 750 cm$^{-1}$ below the excitation. When the monochromator was tuned to observe fluorescence 950 cm$^{-1}$ below the excitation, a lifetime of 30 µsec was obtained. Therefore, the blue fluorescence at $\Delta v_2 = -1$ clearly has a shorter lifetime than other fluorescence in this spectral region. Finally, with 5.4 mtorr of NO$_2$, the fluorescence intensity decreased by roughly a factor of ten either when the laser was tuned off the Q(13) line or when the monochromator was tuned away from the $\Delta v_2 = -1$ fluorescence band.

Several aspects of the experimental results deserve comment. Firstly, the rate constants for collision-induced decay obtained from the slopes of the lines in Fig. 2 are extremely large. These rates are 19.8 and 15.3 µsec$^{-1}$ torr$^{-1}$ for the blue fluorescence excited by the Q(11) and Q(13) lines,
respectively, and 1.6 μsec\(^{-1}\) torr\(^{-1}\) for the red fluorescence. The slower (red) rate may be interpreted as collisional decay into some non-fluorescing level. The faster (blue) rates are roughly 2.5 times the gas kinetic rate and must involve a very efficient process. At present we can only speculate that this process could be rotational relaxation, or perhaps extremely fast electronic energy transfer. Similar highly efficient electronic energy transfer processes have been observed in NO.\(^{11}\)

Finally, the zero-pressure lifetime of the blue fluorescence excited by either the Q(11) or Q(13) lines is found to be 33 ± 4 μsec. A careful examination of the low-pressure fluorescence traces for fast components with lifetimes on the order of 1-3 μsec has shown that such components, if present, form less than 5% of the fluorescence amplitude. Previous investigators\(^8\) have found short components for \(K_a = 0\) states whose amplitude at unspecified pressures was roughly 13% of the broad-band fluorescence. Since our experiment isolates fluorescence specifically from \(K_a = 0\) states, it should be extremely sensitive to such short components if present. Since no evidence for these components was found, we conclude that \(K_a = 0\) lines of the \(^2B_1\) electronic state do not have short lifetimes comparable to the integrated absorption lifetime of 0.3 μsec.\(^3,4\) This fact may indicate that such lines are still appreciably perturbed. However, the mechanism for this perturbation is not immediately obvious. The Renner-Teller effect should not mix \(K_a = 0, ^2B_1\) states with \(^2A_1\)
states, and NO$_2$ lacks the proper vibrational mode ($A_2$) to allow first-order vibronic coupling of the $^2B_1$ and $^2B_2$ states. Perhaps this implies a higher order coupling mechanism.

On the other hand, the fact that these states do stand out in the absorption spectrum and even more so in the excitation spectrum of the $v_2$ fluorescence mode suggests that they are, indeed, unperturbed. Since a lengthening of the lifetime by a factor of 100 is not compatible with essentially unperturbed states, perhaps the oscillator intensity from which a 0.3 µsec lifetime is calculated is due primarily to transitions to states other than the $^2B_1$. It has previously been suggested that the 0.3 µsec lifetime may be that of the $^2B_2$ state. If, in fact, the $K_a = 0$ levels are unperturbed, then the lifetime measured in this experiment may be the true lifetime of the $^2B_1$ electronic state.

ACKNOWLEDGMENTS

We gratefully acknowledge the support of the Energy Research and Development Administration and the National Science Foundation. The laser was purchased with National Science Foundation funds for chemical instrumentation.
REFERENCES

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13. Following the completion of this work we received a communication from S.E. Schwartz and G.I. Senum in which $K_a > 0$, $^2B_1$ states near 442 nm were found to have lifetimes similar to those reported here.
FIGURE CAPTIONS

Figure 1. Experimental apparatus for recording the fluorescence excitation spectrum and measuring the lifetimes of NO₂.

Figure 2. Reciprocal lifetimes for NO₂ fluorescence as a function of pressure. The circles and squares are for resolved blue fluorescence excited by the Q(13) and Q(11) lines, respectively. The triangles are for the unresolved red fluorescence. The insert shows an expansion of the low-pressure region for the blue fluorescence.
Fig. 1
Fig. 2
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