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Observation of infrared–optical double resonance in NO_2[a)]

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Several experiments are described in which infrared–optical double resonance is observed for the first time in NO_2. A cw argon-ion laser (4545–5145 Å) is used to excite molecules to the $^2B_2$ and $^2B_1$ states and a chopped cw CO_2 laser (9.2–10.8 μ) is employed to induce an excited vibronic state transition; detection is through infrared laser-induced amplitude modulation of the visible fluorescence. Double resonance is, in fact, observed at each visible–infrared wavelength pair employed. This effect is studied as a function of laser wavelengths, lateral separation of the two laser beams, and NO_2 pressure, and the modulated fluorescence is spectrally analyzed. These results suggest that isoenergetic collisional transfer may contribute to the observations. In addition, evidence is obtained that the optically excited levels participating in the double resonance have very short zero-pressure lifetimes, $\sim 0.6 \pm 0.2$ μsec.

I. INTRODUCTION

The visible absorption spectrum of NO_2 is an incompletely resolved quasicontinuum which is derived from the transitions $^2B_2$, $^2B_1 \leftarrow \tilde{X}(^2A_1)$, the former containing most of the oscillator strength. It has been intensively examined, both theoretically[1] and experimentally, using both classical spectroscopic[2] and high resolution laser techniques.[3-16] However, despite the great amount of accumulated experimental information, this spectrum remains incompletely assigned; the complexity in analysis is thought to stem from perturbations of levels in $^2B_2$ (and possibly also $^2B_1$) by the nearly isoenergetic, dense manifold of high-lying vibrational levels of the ground state, $\tilde{X}(^2A_1)$. The only definite vibrational assignment in these low-lying excited electronic states has been that of the ν_2 bending mode in $^2B_1$ by Douglas and Huber[2]; Brand *et al.*[7] have also made a tentative assignment of the $^2B_2$ fundamentals. In addition, a state with symmetry $^2A_2$, which has been theoretically predicted at 1.84 eV,[1] remains unobserved, partly because $^2A_2 \leftarrow \tilde{X}(^2A_1)$ is electric dipole forbidden.[17]

Double resonance studies may prove to be of value in the study of NO_2 because they provide a great simplification in the spectral analysis, different selection rules as compared to one-photon probing, and selective excitation of a single velocity group upon absorption of the first photon. Previously, Tanaka *et al.*[8,12,18] and Solarz, Levy and co-workers[19,20] have studied NO_2 rotational structure in both the excited and ground electronic states using microwave–optical double resonance. This paper details an exploratory spectroscopic study of NO_2 using infrared–optical double resonance (IODR) in which an optical photon promotes NO_2 to an excited electronic state, $^2B_2$ or $^2B_1 \leftarrow \tilde{X}(^2A_1)$, and then an infrared photon induces a transition corresponding to absorption or stimulated emission, either within the same electronic state or to a different electronic state.

The results reported here suggest the desirability of additional, more systematic IODR studies, the specific goals of which would be vibrational analysis of the perturbed $^2B_2$ and $^2B_1$ states and experimental characterization of the $^2A_2$ state. The latter aim is feasible because the infrared transitions $^2A_2 \leftarrow {}^2B_2$ and $^2A_2 \leftarrow {}^2B_1$ are both electric dipole allowed and, in fact, theoretical calculations[1] suggest that the former transition has favorable Franck–Condon factors.

In this study a cw argon-ion laser (4545–5145 Å) and a chopped cw CO_2 laser (9.2–10.8 μ) were incident on an NO_2 cell, and the visible sidelight was examined for amplitude modulation at the infrared laser chopping frequency, which would indicate the occurrence of a double resonance. As discussed by Field *et al.*,[21] in an excited state double resonance study the second electromagnetic field (infrared or microwave) can alter the populations of various levels in the optically pumped excited electronic state and can thereby change the observed broadband fluorescence intensity because of a variety of factors: differing radiative decay or collisional quenching rates of the two states involved in the second transition, lessening of optical transition saturation (leading to the absorption and fluorescence of more optical photons), wavelength-dependent quantum efficiency differences for fluorescence detection from initial and final levels and polarization effects. Previous investigations[3-5,8-10,14] have shown that all of the argon-ion laser wavelengths, with the exception of 4545 Å, excite predominantly levels with $^2B_2$ character; Hardwick[15] has noticed that 4545 Å excites a single rovibronic level in $^2B_1$.

The appearance of IODR was surveyed as a function of the many possible infrared–visible wavelength combinations available from these two line-tunable lasers. The argon-ion laser was then forced to oscillate in a single longitudinal mode and the IODR signals were scanned as a function of argon-ion laser mode frequency, at fixed infrared wavelength. In addition, several other observations were made, including (1) the pressure dependence of IODR, (2) the dependence of the double resonance signal strength on the lateral separation of the two lasers (which provides lifetime data), and (3) the spectral composition of IODR fluorescence.

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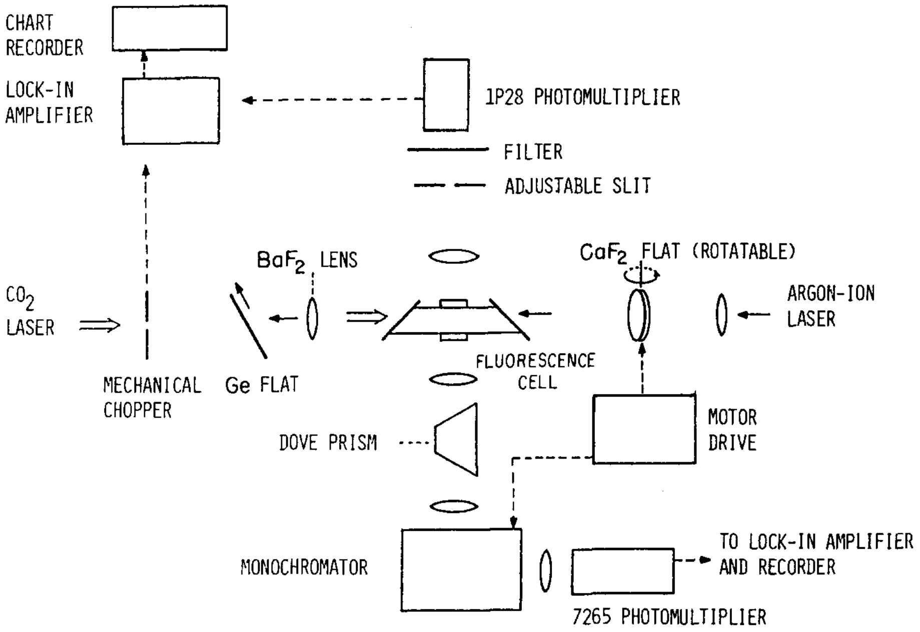


FIG. 1. Experimental arrangement for the double resonance study.

For comparison, analogous experiments were also performed for single visible photon excitation. The results of these experiments are presented in Sec. II, and the implications relating to the spectroscopic and kinetic aspects of IODR in NO_2 are discussed in Sec. III.

II. EXPERIMENTAL OBSERVATIONS

Several experiments were performed using the argon-ion and CO_2 line-tunable cw sources; the various experimental arrangements are diagrammed in Fig. 1. The two counterpropagating beams were superimposed in a fluorescence cell and both focused to 0.1 mm at the same point, adjacent to two side-viewing windows. The CO_2 laser was mechanically chopped at 110 Hz before impinging on the cell; in addition, a thin germanium flat was inserted at Brewster's angle between the CO_2 laser and the cell to prevent visible laser feedback to the cell, which could produce false IODR signals. In the initial studies the argon-ion laser was employed in longitudinal multimode operation. The occurrence of a double resonance was detected as an amplitude modulation (at 110 Hz) in the broad-band visible fluorescence monitored by a 1P28 photomultiplier preceded by a suitable (visible laser absorbing) cut-on absorption filter.

Double resonance fluorescence modulation was, in fact, observed at each optical-infrared wavelength pair chosen, specifically for the $\lambda = 4545$, 4579, 4765, 4880, and 5145 Å argon-ion laser wavelengths with the $P(8) \rightarrow P(38)$ and $R(8) \rightarrow R(34)$ rotational lines in the CO_2 laser 10.4 μ band. Similar signals were also observed with CO_2 laser oscillation in all available lines in the 9.4 μ band. In every case *but one* the infrared laser induced an increase in visible fluorescence at all NO_2 pressures, which was detected as a positively phased signal. For a given visible laser wavelength only a $\pm 20\%$ variation in the degree of modulation of fluorescence was noted for the different infrared wavelengths at equal laser powers. The intensity of the modulated fluorescence was strictly linear with visible laser power to the maximum available power at each wavelength (0.05–1.0 W). The variation of this IODR fluorescence was nearly linear with infrared laser intensity, showing a slight decrease from linearity at higher intensities, 10^5 W/cm^2, corresponding to a power of 10 W. Great care was exercised to insure that feedback did not contribute to these results through visible laser back reflection off the infrared laser optics.

This IODR fluorescence was then analyzed as a function of NO_2 pressure, p, as plotted in Fig. 2, where allowance has been made for the pressure dependence of the visible laser attenuation before reaching the viewing port. For comparison, the kinetic dependence of one (optical) photon fluorescence is also plotted; in this latter case, the fluorescence rises rapidly with pressure and reaches a constant value for $p > 100$ mtorr. On the other hand, the IODR signal rises much more slowly with pressure, reaches a maximum near 1 torr, and decreases at higher pressures. At the optimum pressure of 1 torr, the fractional modulation of visible fluorescence is about 0.2%. The modulation depth of the fluorescence is sensitive to laser alignment, as are the quantitative, but not qualitative, aspects of the kinetic dependence.

There was exactly one wavelength pair which led to much different signals than the others, namely, 4880 Å-$R(12)$, 10.3 μ. As indicated in Fig. 3, kinetic examination indicated that at 100 mtorr the fluorescence modulation changed phase, to negative phase, indicating that the CO_2 laser induced a net decrease in visible fluorescence. The magnitude and sign of the observed signal were very sensitive to the specific infrared laser frequency, as was determined by tuning across the Doppler profile of the $CO_2\,R(12)$ laser line.

These IODR effects were further investigated by inserting a 1 cm thick, 40% reflecting quartz etalon in the argon-ion laser cavity, thereby achieving single longitudinal mode operation. By suitably tilting this 10

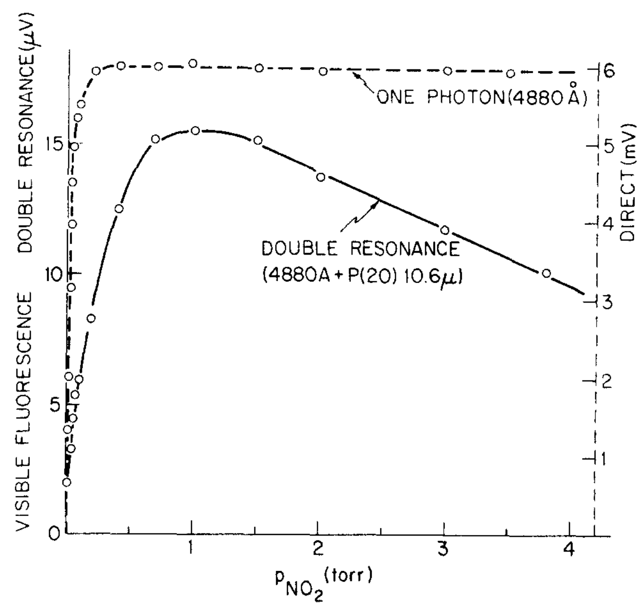


FIG. 2. Pressure dependence of double resonance and single visible photon fluorescence. Allowance has been made for visible laser absorption in the sample cell preceding the viewing ports.

GHz free spectral range etalon, the laser mode frequency was scanned stepwise, with 115 MHz longitudinal mode spacing, across the 8 GHz wide argon-ion laser profile. For *all* wavelength pairs inspected (4880 Å—various CO_2 laser lines), there was a small positively phased IODR signal background which was nearly independent of the visible laser frequency within the scanned laser profile; however, in most cases 1 GHz wide, usually positive, peaks were observed superimposed upon this background. The argon-ion laser scans for several of the infrared lines, in both the 10.4 μ and 9.4 μ bands, were dominated by a single, strong, 1 GHz wide positive resonance, occurring 2 GHz below the 4880 Å linecenter. In the "anomalous" 4880 Å-R(12) 10.3 μ case, a large, 1 GHz wide, negatively phased signal centered 800 ± 300 MHz below the 4880 Å line center was superimposed upon the positive background. The magnitude of this negative peak was about 4 times the background.

An examination of the distance an excited molecule travels before de-excitation can provide both pressure-dependent and independent relaxation rates. The lifetimes of the contributing IODR optically excited NO_2 levels were thus examined for several of the visible-infrared laser pairs by simply observing the fluorescence intensity as a function of lateral displacement of the visible beam relative to the fixed infrared beam. As diagrammed in Fig. 1, a 6 mm thick CaF_2 flat was inserted between the argon-ion laser and the cell, and the angle of incidence was mechanically scanned in time, while the modulated fluorescence detected by the photomultiplier was recorded on a strip chart recorder. In effect, the CO_2 laser focus served as a selective "IODR slit", as only those excited NO_2 molecules both physically present and in the appropriate states (which could interact with the infrared field) produce a signal. Since during a scan the "slit" is stationary, the solid angle of collection of visible fluorescence is constant. The beam displacement was both calculated and experimentally verified as a function of angle, and intensity corrections were made for the angle-dependent reflection off the CaF_2 flat.

The results of an analogous one visible photon diffusion experiment are presented first. The diffusion of electronically excited NO_2 molecules was measured by spatially scanning the argon-ion laser beam, as detailed above, however, with no infrared laser present. In this instance the fluorescence was focused onto a stationary 0.1 mm wide external slit before impinging on the photomultiplier. One expects the spatial dependence of the fluorescence to vary as the convolution of the Green's function solution of the diffusion equation for a line-excitation source, $(S/2\pi D)K_0(r/r_0)$, over the transverse beam profile of the laser; S is the source intensity and $r_0 = \sqrt{D/\gamma}$, where D and γ are the diffusion coefficient and total decay rate, respectively. For pressures greater than about 10 mtorr, at which collisional deactivation, rather than radiative decay, dominates relaxation and at which the mean free path is much shorter than the 1 cm cell radius, $D \propto 1/p$ and $\gamma \propto p$ and the width of profile, r_0, should vary approximately as $1/p$. This predicted gradual broadening with decrease in pressure was observed for pressures down to 10 mtorr[22]; characteristic spatial scans, with multimode 4880 Å excitation, are exhibited in Fig. 4.

In contrast, the spatial behavior of IODR was quite different. Figure 5 shows the dependence of the scans at various pressures for the 4880 Å (multimode)-P(20), 10.6 μ case. As in the one photon example, at high pressures ($\gtrsim$ 5 torr) the observed profile is merely the convolution of the focused visible laser profile and the slit employed, either the CO_2 laser or the mechanical slit. The IODR profile broadens slightly as the pressure is decreased to about 1/2 torr; however, the shape of this profile remains essentially unchanged as the pressure is further decreased to the low pressure observation limit of 23 mtorr. This small spatial broadening at low pressure indicates that the optically excited states involved in the IODR decay rapidly and have a zero-pressure lifetime of about 0.6 ± 0.2 μsec. This

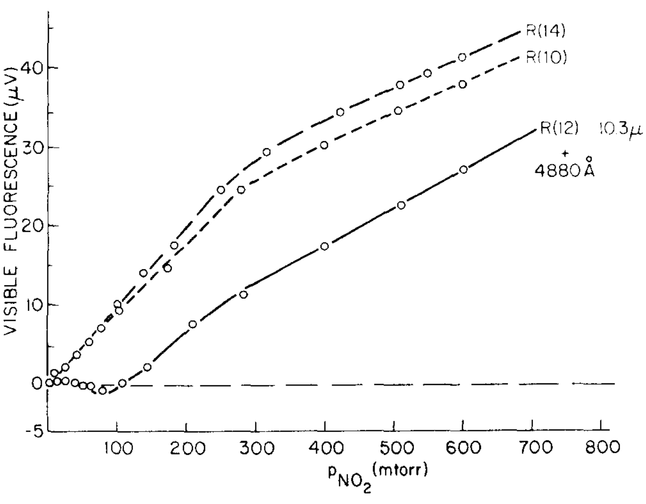
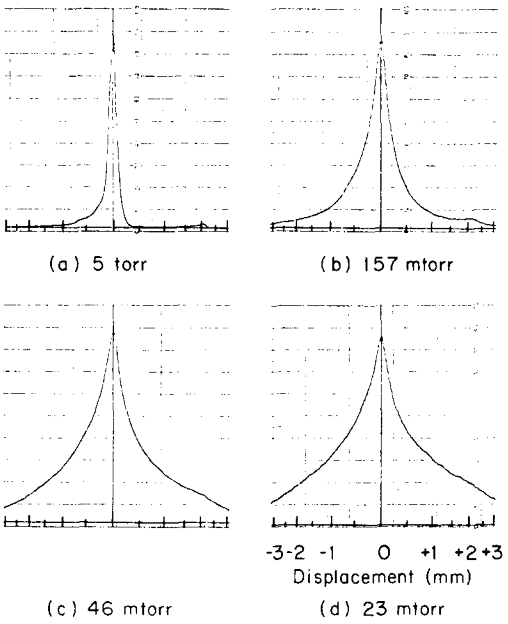


FIG. 3. Pressure dependence of the IODR signals for the anomalous 4880 Å – R(12) 10.6 μ case and for the neighboring CO_2 laser wavelengths.



(a) 5 torr (b) 157 mtorr (c) 46 mtorr (d) 23 mtorr

FIG. 4. Spatial behavior of single visible photon fluorescence, monitored through a stationary 0.1 mm slit as the optical laser was translated.

was determined by convoluting $e^{-r/v\tau}$ over the high pressure profile, where r is the extent of travel, v is the average one-dimensional molecular speed, and τ is this pressure-independent lifetime. Since, in this instance, the mean free path is longer than the extent of IODR broadening, this free-flow expression is employed instead of the Green's function for diffusion. The other typical cases examined exhibited similar behavior; however, the 4880 Å (multimode)-$R(12)$, 10.3 μ case again proved to be exceptional. Figure 5 shows that at 92 mtorr the negatively phased fluorescence, discussed above, occurs only with near-total overlap of the two beams; the corresponding lifetime is again about 1 μsec.

The spectral composition of the double resonance fluorescence was examined in low resolution with multimode operation at 4880 Å. As outlined in Fig. 1, the image of the horizontal fluorescence zone transmitted through a side viewing port was rotated by a dove prism and focused ($f/2$ optics) onto the vertical slit of a 1/2 m monochromator. An RCA 7265 photomultiplier at the exit slit sent the observed signal to a strip chart recorder as the wavelength of the monochromator was linearly scanned in time.

The single visible photon fluorescence spectrum of NO$_2$ has been well investigated.[3] It is known (and verified here) to consist of sharp peaks near the exciting wavelength and at Stokes shifted wavelengths, which are superimposed upon a broad quasicontinuum beginning at the exciting wavelength, peaking at roughly 6000 Å for 4880 Å excitation at 1 torr NO$_2$ and extending to the near infrared. The spectrum of the modulated IODR fluorescence [observed for the cases of 4880 Å multimode, $R(10)$, $R(12)$, and $R(14)$ 10.3 μ] is quite different. In contrast to the one-photon case, the quasicontinuum began at wavelengths shorter than the exciting wavelength, ~4500 Å, peaked approximately at the excitation wavelength, and decreased fairly rapidly at longer wavelengths. In fact, some IODR fluorescence was observed at wavelengths shorter than 4660 Å, which corresponds to the sum of the energies of one infrared and one optical photon.

III. DISCUSSION

A. Origin of the modulated fluorescence

Despite the quasicontinuous, unresolvable NO$_2$ visible absorption spectrum, it is still surprising that modulated fluorescence was observed at each visible-infrared wavelength pair. There are several possible interpretations of these results. One possibility is that of direct, excited-state double resonance, in which the visible photon excites several levels in the low-lying excited electronic states and the infrared transition occurs from these levels; this case was initially described in Sec. I. Alternatively, collisions may relax the optical laser excited levels, and the infrared transition may instead occur from these collisionally populated levels. Collisions might populate nearly isoenergetic levels, that is, other rotational and vibrational levels in the same electronic state or near degenerate levels in other electronic states [$\tilde{X}(^2A_1)$, $^2B_1$(or $^2B_2$), $^2A_2$] or possibly levels at significantly lower energy in the various electronic states. Another possible mechanism that could account for the observations consists of optical photon absorption from a "hot band" in $\tilde{X}(^2A_1)$, followed by an infrared transition. The case of ground state IODR, in which the infrared photon is first absorbed in $\tilde{X}(^2A_1)$ and then a visible photon is absorbed, must also be con-

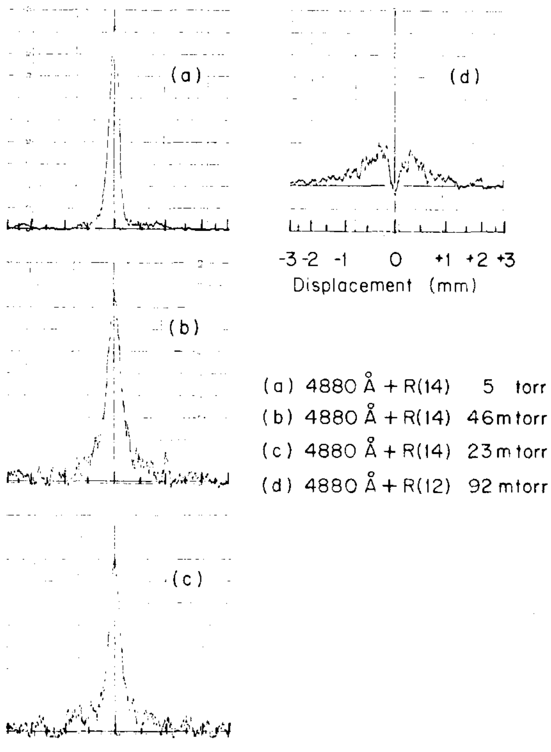


FIG. 5. Spatial behavior of the IODR modulated fluorescence, monitored by laterally displacing the visible laser relative to the CO$_2$ laser.

sidered. Simultaneous absorption of an infrared and an optical photon, i.e., two-photon absorption, is another possible explanation. As noted earlier, feedback effects have been carefully considered and have been found not to contribute to the observations. In addition, the reaction of electronically excited NO_2 with ground state NO_2, in which NO and O_2 are formed,[23] should not interfere with the results. The experimental observations are now analyzed in light of the above possible explanations.

B. Experimental implications

The small fractional modulation in fluorescence indicates that the observations are due to either the interaction of the infrared field with a small fraction of the optically excited molecules, small infrared transition oscillator strengths, or lack of differential sensitivity in the employed detection method.

Visible laser heating of the medium could influence the observations only if hot band absorption were important in the mechanism. Assuming complete $V-T$ equilibration within the beam focus and allowing for thermal conduction to the walls, the maximum possible visible laser-induced temperature rise at the focus is about +50 °C for 1 W of 4880 Å focused on a 1 torr NO_2 sample. If the temperature rise is actually this large *and* if "hot band" absorption were important, the IODR fluorescence vs visible laser intensity behavior would be noticeably nonlinear, having positive curvature; this was not observed. Infrared laser heating is expected to be negligible.

The pressure dependence portrayed in Fig. 2 is easily understood. In the one-photon case the fluorescence intensity at low pressure varies as p since the rate of pumping molecules is proportional to the concentration of NO_2 molecules, while the relaxation is due to radiative decay and transit to the walls, which are pressure independent. Above 100 mtorr, the sidelight intensity is independent of pressure since the decay of excited molecules is then due to bimolecular collisions. (N_2O_4 formation is not important in the pressure regimes of observation.) The IODR fluorescence exhibits a quite different pressure dependence. The relatively slow increase with pressure at low pressure indicates either rapid pressure-independent decay of the intermediate state or rapid transit of visible laser-excited molecules out of the infrared laser focus. The high pressure (> 1 torr) IODR behavior may be explained by first noting that in this regime the concentration of optically excited molecules is independent of p. In single-mode optical excitation a single, homogeneously broadened velocity group is excited and the rate of infrared pumping to the next level is $\propto 1/p$ at line center. For optical-multimode excitation (and if velocity changing collisions fill in the gaps in velocity space) the entire Doppler spectrum is excited and the rate of infrared pumping is then independent of p. In either case, bimolecular collisions relax the infrared excited level so the high pressure IODR fluorescence intensity should vary either as $1/p^2$ (single-mode) or $1/p$ (multimode); an approximately $1/p$ dependence is observed with multimode excitation.[24] This decrease in modulated fluorescence at high pressure discounts the role of two-photon absorption, which instead requires a kinetic behavior qualitatively similar to that of single photon induced fluorescence.

It is impossible to extract quantitative information from this IODR intensity vs pressure curve because the behavior critically depends on the *difference* in both the pressure-dependent and pressure-independent decay rates of the two levels involved in the infrared step and also on the spectral response of the photodetector. An order of magnitude estimate of the pressure-independent lifetime may be obtained assuming that (1) the observed IODR signal is due only to the different spectral sensitivity of the photodetector at the wavelengths of fluorescence from the initial and final levels involved in the infrared step, (2) at zero pressure the two levels involved in the infrared step radiate at the same rate; this rate could be different from the lifetime observed for the major component of single-photon fluorescence, and (3) all NO_2 levels are relaxed by collisions at the same rate. Under these conditions it is possible to show that the peak of the IODR curve (1 torr) occurs at a pressure at which the collisional and pressure-independent decay rates are equal. Also, single-photon fluorescence reaches its half-maximum height when this condition is fulfilled for its levels (at ~15 mtorr). If collisions are assumed to relax all levels at equal rates, the pressure-independent lifetime of the IODR levels is about 65 (≅1 torr/15 mtorr) times shorter than that for one-photon excitation. This latter lifetime is approximately 28 μsec, due to both the "bulk" radiative lifetime of ~75 μsec[25,26] and the transit time to the walls of ~45 μsec, thus implying roughly 0.4 μsec for the lifetime of the IODR levels.

The observation of positive and negative peaks in the single mode argon-ion laser scans indicates that the observed IODR modulated fluorescence could in principle be assigned. The appearance of a positive peak 2 GHz below the 4880 Å line center for several nonadjacent CO_2 laser wavelengths suggests that after a *specific* $^2B_2$ level is optically excited, this population may be distributed to a specific and distinguishable group of nearby levels by collisions. Approximately 40 rovibronic levels are excited by 4880 Å multimode excitation, and about five are simultaneously excited by any given single mode[27]; therefore, it is highly significant that IODR peaks appear at only a few longitudinal mode frequencies in the scan. The positively phased peaks in the 4880 Å single-mode scans and the positively phased fluorescence observed with most visible–infrared pairs suggest that either (1) most transitions are to states of shorter radiative lifetimes or smaller collisional relaxation cross sections, (2) the visible transition is heavily saturated, or (3) that more transitions are infrared absorptions that emissions, and the subsequently emitted visible photons are more efficiently detected than those from one-photon fluorescence. A plausible explanation involves only the first and third mechanisms, as the modulated fluorescence is not observably saturated under usual operating pressures and laser powers. In the anomalous 4880 Å-$R(12)$, 10.3 μ combination, the negative peak (single mode) and signal (multimode) suggest that the infrared step might be a transition to a state with a long radiative lifetime, such as the $^2A_2$ electronic state which cannot fluoresce in the visible.

The IODR spatial scans of Fig. 5 have three implications. First, they show that the slow rise with pressure near zero pressure portrayed in Fig. 2 cannot be due to the transit of optically excited molecules out of the infrared beam focus, because this possibility falsely predicts a significant increase in spatial width at low pressure. Second, since the fluorescence in the wings of the spatial plots of single-photon fluorescence (Fig. 4) derives primarily from nonisoenergetic vibronic levels which are populated by significant collisional energy removal from the directly laser-excited levels, and since the IODR spatial profiles are much narrower than the single-photon scans, nonisoenergetic levels apparently do not contribute significantly to the observed IODR fluorescence. This is further confirmed by the single-mode IODR scanned resonances, because any state selectively produced by single mode excitation would not be conserved after several energy relaxing collisions, and also by the IODR fluorescence spectral analysis, as discussed below. Third, the microsecond decay of the intermediate IODR states implies that the infrared transition occurs in the excited state since vibrational levels populated by infrared absorption in the ground state are expected to have much longer lifetimes, >1 msec.

Ground state infrared absorption is not expected to contribute to the observations also because the ground state vibrational fundamentals are far removed from the 10 μ spectral region and ambient temperature hot band absorption combination bands would be too weak to account for the observed fraction of fluorescence modulation. If laser heating increased the contribution of infrared hot band absorption, then the modulated fluorescence would increase faster than linearly in visible or infrared laser power, contrary to the results of this study.

The 0.6 μsec pressure-independent lifetime is probably due to either radiative decay or intramolecular relaxation of the optically excited intermediate IODR levels; at present, it is impossible to attribute this decay solely to either one of these two possibilities. The radiative lifetime of optically excited NO_2 under broad-band excitation is about 75 μsec (4000–6000 Å),[25,26] much longer than that expected on the basis of the integrated absorption oscillator strength, 0.3–1.5 μsec.[28,29] With monochromatic laser irradiation some very short, as well as, multiple (nonexponential) lifetimes ranging from 0.5–260 μsec (4500–6120 Å)[6,29–34] have been reported. Solarz and Levy[19] measured a 3.39 ± 0.36 μsec zero pressure lifetime for the level excited by a single-mode argon-ion laser participating in microwave–optical double resonance. The anomalies in the NO_2 lifetime observations and spectra have been attributed to perturbative mixing of the Born–Oppenheimer eigenstates, $^2B_2$ and $\tilde{X}(^2A_1)$. These processes have been discussed, in relation to NO_2, by Douglas,[35] Butler *et al.*,[36] Paech *et al.*,[32] Brand *et al.*,[37] and by Donnelly and Kaufman,[29] and, in general terms, by Bixon and Jortner.[38] Absorption of an optical photon could prepare the molecule in a superposition of several eigenstates, which initially appears to be a level with mostly $^2B_2$ character; this superposition may dephase more rapidly than the radiative decay of the individual eigenstates. The 0.6 μsec lifetime observed here would require several dephasing levels to occur within a ~0.5 MHz energy spread.

As discussed in the previous section, the spectral composition of single-photon fluorescence consists of Stokes shifted lines superimposed upon a quasicontinuum which peaks at about 6000 Å for 4880 Å excitation. The location of this peak is thought to be a function of collisional relaxation, the Franck–Condon factors for emission, and the spectral response of the photodetector. (For the *S*-20 response of the employed photomultiplier sensitivity decreases rapidly for $\lambda > 7000$ Å.) Since the IODR spectral peak does not occur within 1000 cm^{-1} of the single-photon peak, this confirms that the infrared transitions in IODR do not occur in excited vibronic levels that have been significantly relaxed in energy after visible laser excitation (assuming similar Franck–Condon factors). Also, the shift to shorter wavelengths in the IODR spectrum suggests that a large fraction of the IODR signal corresponds to infrared photon *absorption* rather than stimulated emission. The appearance of some fluorescence at wavelengths shorter than 4660 Å, corresponding to the sum of the two photons, may be due to hot-band optical excitation, followed by infrared absorption. This mechanism would account for both the observed blue shift and the infrared laser-induced increase in detected fluorescence. Note that even after the absorption of both an optical and an infrared photon, the molecule is well below the dissociation energy, which corresponds to the onset of the predissociation-induced diffuse absorption spectra at 3979 Å.

C. Models for excited state IODR

Several of the proposed mechanisms listed earlier in this section are inconsistent with experimental findings. One may conclude that the observed signals are due to excited state double resonances; however, collisions may be important. The detailed pathways of collisional relaxation in optically excited NO_2 are as yet unknown; however, the general flow of energy may be analyzed in two steps. First, excitation is probably rapidly transferred from the optically populated levels to nearly isoenergetic rotational and vibrational levels within the same electronic state ($^2B_2$), as well as to the other electronic states [$\tilde{X}(^2A_1)$, $^2B_1$, $^2A_2$]. Since $^2B_2$ appears to be heavily perturbed by $\tilde{X}(^2A_1)$, NO_2 which has been excited to specific levels of predominantly $^2B_2$ character is rapidly collisionally transferred into isoenergetic $\tilde{X}(^2A_1)$ levels.[39] The second step in relaxation is due to energy removing collisions. The studies of Schwartz and Johnston[25] and of Keyser *et al.*[40] suggest that energy relaxation occurs predominantly down the $\tilde{X}(^2A_1)$ manifold, with about 1000 cm^{-1} (corresponding to about an average vibrational quantum) lost per gas kinetic collision. The experimental results of this study suggest that the observed effects do not involve the interaction of an infrared photon with an NO_2 molecule that has been significantly relaxed in energy after absorbing an optical photon. Perhaps IODR absorption and emission do occur from these energy relaxed levels; however, the resultant effects could cancel in the present detection scheme.

The most likely possibility is that the observed signals are due to absorption of an optical photon (possibly from a vibrationally excited level), followed by an infrared transition from either the directly populated level or from a closely coupled, nearly isoenergetic level. One may attempt to differentiate between collision- and non-collision-induced processes by considering the statistically calculated density of states. Modeling NO_2 as a threefold degenerate oscillator after Schwartz and Johnston,[25] the vibrational level spacing in $^2B_2$ at 2.54 eV (4880 Å) is about 45 cm^{-1}, whereas in $\tilde{X}(^2A_1)$ it is about 7 cm^{-1} at this energy. Multimode laser radiation at 4880 Å having a spectral width of 8 GHz excites about 40 different levels in $^2B_2$.[27] Perpendicular rotational selection rules for a prolate symmetric top, $\Delta N = 0, \pm 1$, $\Delta K = \pm 1$, are employed to calculate the possible number of coupled infrared transitions. Considering first only vibrational transitions in $^2B_2$, and assuming that transitions are allowed between any two vibrational levels in resonance, these rotational selection rules, and the possibility of both infrared absorption and emission, the average "effective" infrared transition density for IODR is $45\ cm^{-1}/40 \cdot 6 \cdot 2 = 2.8$ GHz. An analogous calculation for $^2B_2 \leftarrow \tilde{X}(^2A_1)$ transitions yields 0.4 GHz, while $^2A_2 \leftarrow {}^2B_2$ leads to a spacing greater than 5 GHz. This average spacing of infrared transitions is much larger than the infrared Doppler width of 50 MHz and also exceeds any expected collisional or radiative broadening. Power broadening could explain a "direct IODR continuum" within $^2B_2$ only if $\mu_I E_I/h > 2.8$ GHz, where μ_I and E_I are the infrared transition moment and laser electric field strength. This would require μ_I to be greater than 1 D for combination bands in $^2B_2$, and this is impossible; similarly, an impossibly large matrix element would be needed for $^2B_2 \leftarrow \tilde{X}(^2A_1)$ infrared transitions. Such strong infrared transitions are contrary to the observations since they would imply severe infrared saturation.

The actual transition density may be somewhat larger than that calculated above because of relaxation of the strict prolate top selection rules, vibrational level anharmonicity, and hyperfine splittings; however, the available density still appears to be too small to explain the observed results in terms of direct, collision-free double resonance. Allowing complete rotational level equilibration greatly increases the available density of transitions by a factor of the rotational partition function,

$$\sqrt{\pi (k_B T)^3 / B^2 A}\ ,$$

where A and B are the rotational constants for a prolate top. Employing the $\tilde{X}(^2A_1)$ values for A and B yields a rotational partition function of 4400 at room temperature.[41] This suggests an effective spacing of 100 kHz in $^2B_2 \leftarrow \tilde{X}(^2A_1)$ transitions, sufficiently small to acount for the observation of IODR for every combination of argon-ion and CO_2 laser lines.

Both the direct and isoenergetic collision-induced IODR models are supported by the experimental results; the latter process is the more plausible because of the calculated density of transitions. Though the observed background IODR quasicontinuum may involve collisional population of many rotational and vibrational levels in $^2B_2$ and of the other three electronic states, the peaks observed in the single-mode scans may involve a more selective process. The general increase of fluorescence induced by the infrared field may be explained by optical excitation to $^2B_2$ levels, followed by collisional transfer to isoenergetic $\tilde{X}(^2A_1)$ or $\tilde{X}(^2A_1)$-diluted $^2B_2$ levels, with subsequent infrared transitions to $^2B_2$ levels.

IV. UNANSWERED QUESTIONS

The rather surprising experimental observation of infrared—optical double resonance at *each* attempted laser wavelength pair suggests that partial collisional relaxation of the optically excited state accounts for the observed behavior. Extensions of this double resonance technique should elucidate the spectroscopic and both inter- and intra-molecular kinetic features of NO_2.

Within the framework of this study there are several unanswered questions involving the apparent 0.6 μsec "radiative" lifetime of the intermediate IODR state, the resonance 2 GHz below the 4880 Å line center in the single-mode argon-ion laser scans, and the possible excitation of a $^2A_2$ level with 4880 Å-R(12), 10.3 μ irradiation. Due to the limited versatility of the line tunability of the two employed lasers, this study is exploratory in nature, and no definite spectral assignments are made. Unresolved questions may be answerable using tunable infrared and visible sources. Such a study is presently in progress. The relative contributions of direct and collision-induced IODR processes should be apparent by their relative intensities. Excited vibronic state assignments should be possible by employing tunable infrared lasers at various interesting wavelengths, such as the predicted $^2B_2$ fundamentals as well as near 10 μ.

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