MULTIPHOTON VIBRATIONAL PUMPING OF OPTICALLY PREPARED NO_2 MOLECULES[*]

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Reported is the collisionless infrared multiphoton excitation of NO_2 molecules initially prepared in an electronically excited state. From the shape of the infrared induced blue-shifted fluorescence spectrum the probability distribution $P(n)$ for the net absorption of n photons has been deduced.

The shape of the probability distribution function $P(n)$ for n-photon infrared excitation of molecules has been the subject of lively discussion in the literature [1–3]. In this work, we report the observation of infrared multiphoton vibrational excitation of a molecule initially prepared in an electronically excited state. By monitoring the transient visible fluorescence spectrum, we determined the energy distribution function produced by collisionless infrared multiphoton pumping.

Vibrational excitation of an electronically excited molecule has been reported earlier [4] for the ^3A_u state of biacetyl. That excitation involved a collisional energy exchange between vibrationally excited ground state molecules and optically prepared triplet molecules. The present experiment involves single photon optical excitation of NO_2 molecules from the $^2A_1$ ground state to high levels of the strongly mixed $^2B_2$–$^2A_1$ vibronic manifold, followed by direct infrared multiphoton pumping with a very short CO_2 laser pulse. This work was prompted by an earlier report [5], in which weak double resonance signals were observed in NO_2 molecules exposed simultaneously to cw Ar^+ and CO_2 laser beams.

The experimental arrangement is shown in fig. 1a.

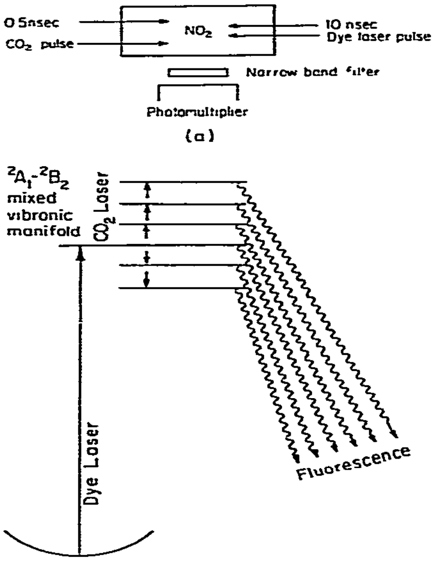

Fig. 1. (a) Schematic of the experimental arrangement. (b) Schematic diagram of pumped energy levels.

A gas cell of NO_2 at a pressure ≈ 250 mTorr is subjected to a 0.5 ns CO_2 laser pulse and an antiparallel 10 ns dye laser pulse which overlaps the central uniform intensity region of the infrared beam. The delay between the two pulses can be adjusted from 0–30 μs with a 30 ns jitter. The fluorescence pulse from the excited NO_2 molecules is imaged onto a photomultiplier tube through narrow bandpass filters

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and recorded on a dual-beam oscilloscope. Fig. 1b illustrates the energy levels participating in the experiment.

A typical series of fluorescence signals generated by the CO_2 laser *following* dye laser excitation is shown in fig. 2. A small portion of the scattered visible laser pulse leaked through the narrow band filter and was recorded at the left edge of the lower trace. The fluorescence pulse in the lower trace occurs at the instant of the delayed CO_2 pulse which is on the upper trace of fig. 2. As can be seen the amplitude of the generated fluorescence decreases at a characteristic rate k_0' as the delay between the two pulses increases. No signals are obtained when the infrared pulse *precedes* the visible pulse. While ordinary visible excitation leads only to Stokes-shifted fluorescence, CO_2 laser induced signals are detected at frequencies blue-shifted with respect to the dye laser frequency ω_0. The spectral width of the induced fluorescence depends on both the CO_2 laser's energy fluence and intensity. Fluorescence signals have been recorded at frequencies blue-shifted from ω_0 by energies up to 5 times the CO_2 photon energy. The induced fluorescence spectrum is shown in fig. 3.

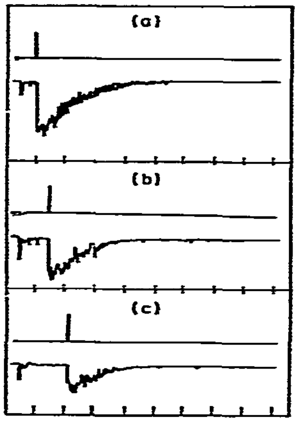

Fig. 2. Upper trace: infrared laser. Lower trace: induced fluorescence signal at 470 nm following dye laser excitation at 502 nm. Delays are (a) 250 ns, (b) 500 ns, (c) 750 ns. Time scale 500 ns/division.

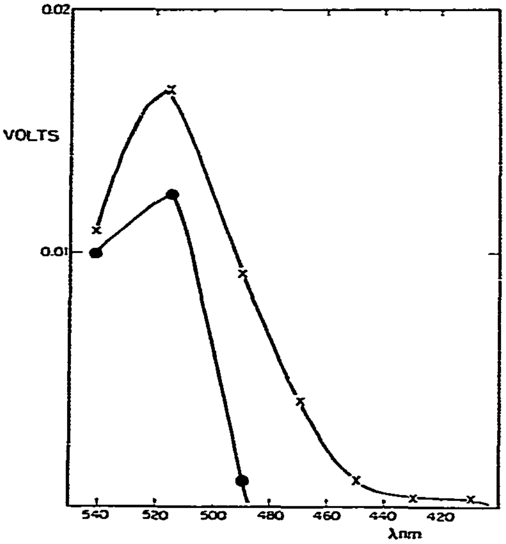

Fig. 3. Dots: ordinary fluorescence spectrum excited by dye laser at 502 nm. Crosses: prompt spectrum induced by CO_2 laser following dye laser excitation.

The relaxation features exhibited by the multiphoton induced amplitude and fluorescence decays are comparable with the decays of ordinary fluorescence signals. Our study of the ordinary fluorescence decay can be summarized as follows:

(a) The fluorescence decay times measured at pressures exceeding 100 mTorr scale inversely with the pressure.

(b) These decay times depend strongly on the observation frequency ω. When fluorescence is studied near the excitation frequency ($\omega_0 - \omega \approx 500\ cm^{-1}$), a quenching rate $k_0 \approx 5.5 \times 10^6\ s^{-1}\ Torr^{-1}$ is measured for excitation wavelengths between 400 nm and 500 nm. As the observation frequency is shifted further to the red, the decay rate decreases. For example, a quenching rate $k = 1.3 \times 10^6\ s^{-1}\ Torr^{-1}$ is observed for 540 nm emission while exciting at 421 nm.

The decay of fluorescence observed at frequencies near ω_0 represents the collisional relaxation of the sharp vibronic distribution prepared by the optical pulse into lower vibronic levels. The longer decay times observed at red-shifted frequencies are due to the larger number of successive vibrational decays required to deactivate the molecules. Fluorescence is observed as long as the collisionally relaxed NO_2 molecule remains in the energy region between $\hbar\omega$ and $\hbar\omega_0$. The decay rates reported in this work are similar to those reported and explained by Donnelly et al. [6].

The decay rates exhibited by the blue-shifted CO_2 induced fluorescence signals also scale with pressure. The measured decay rates vary between 0.6 k_0 and k_0, with the latter value obtained at low CO_2 laser fluences. The increase of lifetime with fluence is related to increased population in levels which require successive collisional events for complete deactivation. The amplitude versus delay relaxation measurements exhibit the same features. While the fluorescence decay monitors emission from multiphoton excited molecules with energy $> \hbar\omega$ the amplitude decay monitors the population of NO_2 molecules still capable of being excited by a multiphoton process to an energy $> \hbar\omega$. Typical values for k_0' of 0.65 k_0 and 0.95 k_0 were obtained for the amplitude decay when the observation frequency corresponded to blue-shifts of one and two CO_2 photons, respectively.

A comparison of the shape of the prompt (<30 ns delay) collisionless infrared induced spectrum with the ordinary fluorescence spectrum permits us to extract the absolute probability $P(n)$ for an n-photon absorption event. The distribution function $P(n)$ may also be regarded as an energy distribution function and written as $P(E_n) = P(\hbar\omega_0 + n\hbar\omega_1)$, where $P(E_n)$ is the probability of occupation of that group of levels with energy near $E_n = \hbar\omega_0 + n\hbar\omega_1$ and $\hbar\omega_1$ is the photon energy of the infrared laser. In what follows, we make the *important* assumption that the prompt fluorescence spectrum depends only upon the populations $P(E_n)$ and not upon the method of producing those populations. Then,

$$F(\omega) = \sum_{n=-\infty}^{\infty} A(\omega, E_n) P(E_n), \qquad (1)$$

where $F(\omega)$ is the prompt fluorescence signal observed at frequency ω, and $A(\omega, E_n)$ is the fluorescence spectrum produced by a population in that group of energy levels near E_n. In general, $n = 0, \pm 1, \pm 2, \ldots$ corresponding both to emission and absorption of infrared photons. In practice, only a finite group of levels have non-zero population and only a finite number of fluorescence observation frequencies ω_m were monitored. Then eq. (1) can be rewritten:

$$F(\omega_m) = \sum_n A(\omega_m, E_n) P(E_n),$$

which is in the form of a vector equation with matrix elements $A_{mn} \equiv A(\omega_m, E_n)$. The matrix of coefficients A_{mn} can be measured one column at a time by performing the following auxiliary experiment using only visible light: A dye laser is tuned to photon energy E_n and its absorbed energy is measured. This determines a population $P(E_n)$. This population along with the vector of fluorescence signals observed under this condition determines a column of the matrix A_{mn}. Repeating this procedure for different E_n determines the full matrix. With a knowledge of the elements A_{mn}, the matrix can be inverted to give

$$P(E_n) = \sum_m (A_{mn})^{-1} F(\omega_m). \qquad (2)$$

If the fluorescence spectrum is known in sufficient detail the populations producing it can be calculated from (2). As a matter of choice, the observation frequencies were selected from the formula:

$$\omega_m \approx \omega_0 + m\omega_1 - 500\ \mathrm{cm}^{-1}.$$

Fig. 4 shows the population distribution resulting from the multiphoton infrared excitation of NO_2 molecules optically prepared by 502 nm dye laser pulses. The CO_2 laser depletes the zeroth level and produces a falling distribution on the high energy side. Due to the small changes in the ordinary Stokes-

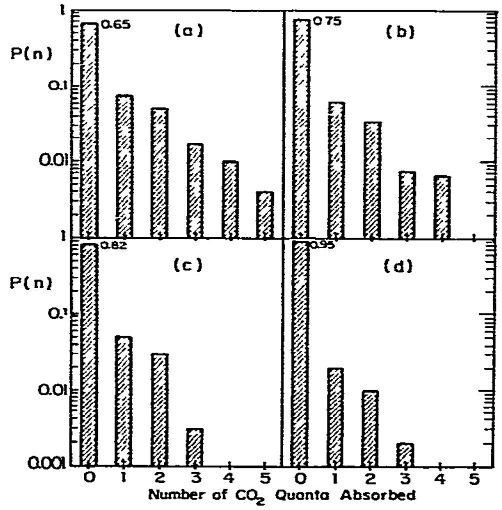

Fig. 4. Histograms of probability $P(n)$ for the net absorption of n photons. (a) 0.5 J/cm^2, (b) 0.3 J/cm^2, (c) 0.2 J/cm^2, (d) 0.1 J/cm^2.

shifted fluorescence signals, the populations at energies less than $\hbar\omega_0$ could not be determined. Presumably a rather symmetrical distribution falling off at lower energies is established.

This procedure for determining $P(n)$ is subject to the very strong assumption that the fluorescence spectrum from levels near E_n is the same whether produced by single photon or multiphoton excitation. Obviously, the selection rules and the precise levels populated may be quite different for the two processes. Nevertheless, the fluorescence spectrum is hardly affected by this difference due to averaging caused by the 1 Å bandwidth of the dye laser and the 50 Å bandwidth of the fluorescence filters. If the differences in fluorescence spectra were important in our case, then we would have seen a fast collisional scrambling signal similar to what was observed by Donnelly et al. [6], but contrary to our observations.

A qualitative survey of the wavelength dependence of the CO_2 laser interaction with optically prepared NO_2 molecules has also been carried out. Blue-shifted fluorescence was observed when tuning over the 9.6 μm and 10.6 μm CO_2 laser lines or tuning the dye laser between 450 nm and 500 nm. This insensitivity to wavelength is surprising in view of the low density of vibrational states of the triatomic NO_2. It implies that exact resonances are probably unnecessary for multiphoton excitation. Indeed infrared multiphoton dissociation has recently been reported in the triatomics OCS [7] and SO_2 [8].

In spite of the rather moderate density of states, a stochastic rate equation approach [9] may describe the temporal evolution of the population $P(n)$. If so, the evolution can be regarded as a random walk along the energy axis with steps of one photon each.

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References

[1] E.R. Grant, P.A. Schultz, Aa.S. Sudbo, Y.R. Shen and Y.T. Lee, Phys. Rev. Letters 40 (1978) 115.

[2] V.S. Letokhov and E.A. Ryabov, in: Laser-induced processes in molecules, eds. K.L. Kompa and S.O. Smith (Springer, Berlin, 1979).

[3] J.C. Stephenson, D.S. King, M.F. Goodman and J. Stone, J. Chem. Phys. 70 (1979) 4496.

[4] I. Burak, T.J. Quelly and J.I. Steinfeld, J. Chem. Phys. 70 (1979) 334.

[5] I.P. Herman, A. Javan and R.W. Field, J. Chem. Phys. 68 (1978) 2398.

[6] V.M. Donnelly, D.G. Keil and F. Kaufman, J. Chem. Phys., to be published.

[7] D. Proch and H. Schröder, Chem. Phys. Letters 61 (1979) 426.

[8] S.E. Bialkowski and W.A. Guillory, Chem. Phys. Letters 60 (1979) 429.

[9] J.G. Black, E. Yablonovitch, N. Bloembergen and S. Mukamel, Phys. Rev. Letters 38 (1977) 1131.