

SPECTROSCOPIC INVESTIGATION OF THE RESPONSE OF THE $\text{NO}_2\text{-N}_2\text{O}_4$ CHEMICAL SYSTEM TO OPTICAL LASER PUMPING

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(Received October 14, 1986)

Summary

An argon laser beam was used to perturb the $\text{NO}_2\text{-N}_2\text{O}_4$ chemical system. The perturbation was monitored, in different experiments, with the laser-induced fluorescence and the IR optical double-resonance (IODR) techniques. The expected quantum perturbations which involve specific rotational levels in NO_2 , $\tilde{X}^2\text{A}_1$ were observed. Unexpected chemical effects which involve the ground state concentration of both species and which are attributed to the response of the chemical equilibrium to the optical perturbation were also observed. The IODR results are discussed with the help of a model based on the Beer-Lambert law, which allows the role of the chemical response to be demonstrated.

1. Introduction

Many publications are devoted to the study of NO_2 . They demonstrate the interdisciplinary interest connected with the study of this molecule, which appears to have an important role in various fields such as spectroscopy [1], molecular dynamics [2], the environment [3] and space research [4].

It is well known that the chemical system to be considered when dealing with NO_2 also includes the dimer N_2O_4 which is always present because of the existence of the chemical equilibrium $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$. Although the amount of the coexisting dimer is large, e.g. 3% at 3 Torr and 25 °C, the potential influence of the chemical equilibrium on the light-induced processes in NO_2 is barely mentioned in the literature. Attempts have been made to study this influence but it could not really be demonstrated [5]. It is our

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aim to show that the entire chemical system has to be considered in order to understand properly the light-induced processes in NO_2 .

The present study is a laser investigation of the $\text{NO}_2\text{-N}_2\text{O}_4$ chemical system. This contribution is concerned with the spectroscopic interpretation of the results. We used the visible and UV fixed-frequency argon laser lines in order to perturb the system. The effects of this optical pumping on the molecules in their ground electronic states were assigned, using literature data and new results based on the laser-induced fluorescence (LIF) technique. These effects were monitored with the help of the IR optical double-resonance (IODR) technique. The use of a line-tunable IR CO laser for these latter experiments allowed us to probe NO_2 and N_2O_4 as well as the NO formed in photodissociation reactions. Experimental details are provided in Section 2. The experimental results are presented and correlated with the literature data in Section 3. The two qualitative interpretations, presented respectively in Sections 4 and 5, demonstrate the role of the chemical equilibrium in the response of the $\text{NO}_2\text{-N}_2\text{O}_4$ system to the optically-induced perturbation. The microscopic and macroscopic effects of the perturbation, together with some of the kinetic mechanisms induced by the optical pumping and responsible for the double-resonance observations, are discussed in Section 6.

2. Experimental procedure

For most of the experiments reported here, the gas NO_2 (Matheson, 99.5% purity) was allowed to flow slowly into a cell at room temperature and at a total pressure of 1 Torr for the LIF experiments and at 3 Torr for the IODR experiments. The higher pressure conditions were needed in order to gain some sensitivity in the detection of N_2O_4 . They correspond to partial pressures of 2.9 Torr NO_2 and 0.1 Torr N_2O_4 according to the value of the equilibrium constant

$$K = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = 8.8 \text{ atm}^{-1} \equiv 215 \text{ mol}^{-1} \text{ l} \quad (1)$$

where the constant given in the literature [6] is also expressed in concentration units. The flow conditions were preferred because they reduced the importance of side reactions such as those connected with the formation of NO (see Section 3).

Three lasers were used.

(i) The first was an argon laser (Spectra Physics 171) which could oscillate in multimode operation, individually on each of the nine visible lines from 4545 to 5145 Å, or multiline on all four UV lines between 3336 and 3638 Å. The maximum output power for each visible line varied between 1.5 W (4658 Å) and 7 W (5145 or 4880 Å); up to 2.4 W was available in the UV.

(ii) Another was a continuous wave (CW) argon laser (Spectra Physics 165) fitted with an etalon, which could oscillate in monomode operation, individually on each of the nine visible laser lines. The monomode operation was monitored with a spectrum analyser;

(iii) The third was a home-made CW CO IR laser of sealed-off design [7] which delivers some 90 laser lines between 1590 and 1790 cm^{-1} , the region of primary interest in the present work. The output power of the individual laser lines ranged between a few milliwatts and several hundred milliwatts, in multimode operation, as measured with a Laser Instruments 154 power meter. The CO laser lines due to the $^{12}\text{C}^{16}\text{O}$ or $^{13}\text{C}^{16}\text{O}$ compounds were identified with a spectrum analyser and their wavenumbers were taken from ref. 8.

2.1. LIF experiments

The experimental procedure used for the LIF experiments has been fully described in a preliminary report of this work [9], and only the main trends of the procedure will be reported here.

The fluorescence induced by each of the visible lines due to laser (i) was photographed at medium resolution using a 2 m Jarrel-Ash spectrograph. The wavelengths of the lines were measured on the photographic plates using the iron spectrum as reference.

The fluorescence induced by each of the visible lines and by the UV lines was also recorded photoelectrically using a 2 m monochromator. Investigations were performed using laser (ii), *i.e.* a monomode excitation, and a microprocessor system allowing the monochromator to be driven semiautomatically. The fluorescence doublets or triplets were identified and assigned, with the help of the measured line wavelengths and of literature constants [10], according to the usual procedure described in ref. 11.

2.2. IODR experiments

Although most of the experimental details have already been presented [12], it seems important for a better understanding of the results and of their interpretation to provide a full description of the procedure. Figure 1 presents the experimental set-up used for the IODR experiments. The beam of the high power laser (i) was focused on the chopper and then entered the cell perpendicular to the IR CO beam, defining in the CO beam an interaction volume that can be approximated by a cube with a side of length $l = 0.5$ cm with the visible beam and $l = 0.07$ cm with the UV beam. IODR signals were observed by monitoring the power variations induced by the optical radiation in the IR beam with a liquid-nitrogen-cooled Au-Ge detector and a lock-in amplifier (LIA) referenced to the chopping frequency (300 - 700 Hz). Searches were made for IODR signals for the full range of $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}$ IR lines for each argon laser line.

The various experimental conditions, such as the pressure and flow conditions, the chopping frequency and the laser power, were varied in

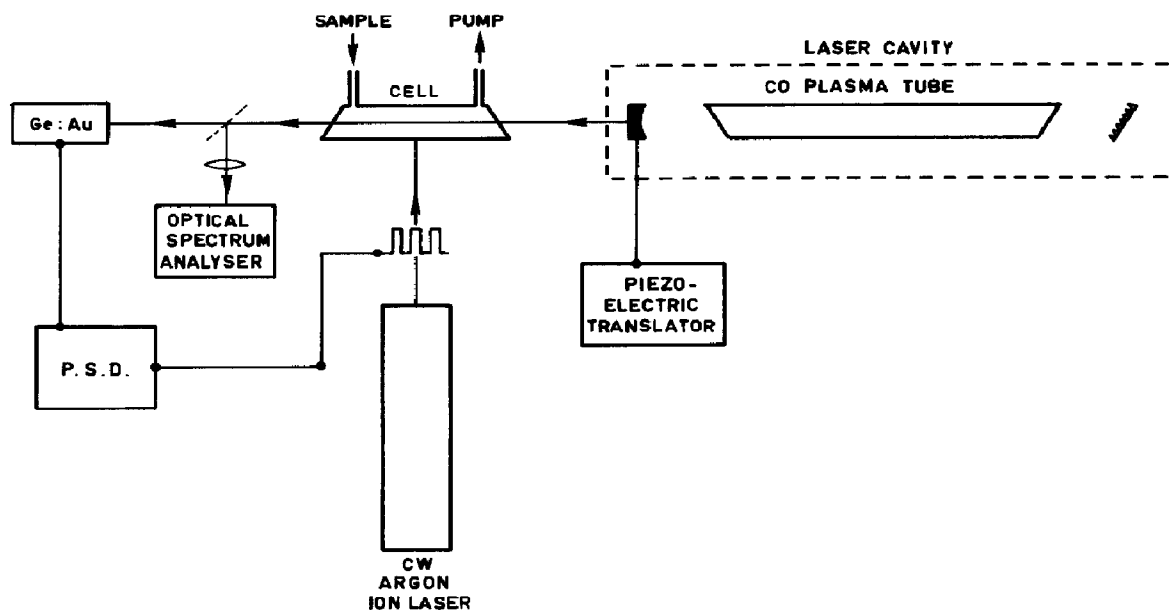


Fig. 1. Experimental set-up used to observe IR optical double-resonance signals in NO_2 - N_2O_4 with CW fixed frequency CO and argon lasers.

order to characterize their influence on the observed signals. Double-resonance experiments were also performed with laser beams overlapping along the full length of the cell, or in the presence of foreign gases or in the CO laser cavity using monomode IR and visible laser beams. These experiments will not be detailed. Their results will be reported only when they add some significant information to this spectroscopically orientated investigation.

2.3. IR absorption coefficients

The absorption coefficient ϵ at each CO laser line was calculated using the Beer-Lambert law

$$I_1 = I_0 \exp(-\epsilon L c_1) \quad (2)$$

where c_1 is the partial concentration of the absorbing species, by measuring the power of the IR beam passing through the cell ($L = 26$ cm) in the absence (intensity I_0) and in the presence (intensity I_1) of the sample at 3 Torr total pressure. These measurements were performed in the absence of any visible excitation.

3. Experimental results

The various absorption processes monitored in the present study are summarized in Fig. 2. Each of the steps detailed in Fig. 2 and characterized by a number x will be specifically referred to in the text in terms of step x .

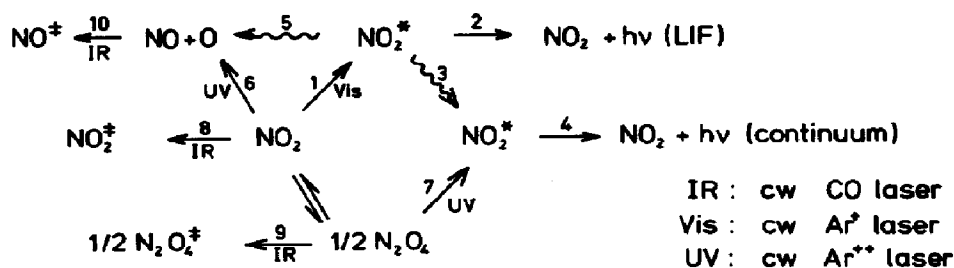


Fig. 2. Representation of the various absorption, emission and photodissociation steps monitored in the NO-NO₂-N₂O₄ chemical system.

TABLE 1

Assignment of the rotational levels of the NO₂ molecule in its ground electronic state belonging to transitions in close coincidence with the visible argon laser lines (electron spin assignments are omitted)

λ_{Ar^+} (Å)	$(J_{K_a K_c})_i$	Reference (see text)
4545	12 _{1 11} ; 6 _{5 1} , 7 _{5 3}	15; 23
4579	10 _{0 10} ; 10 _{1 9}	26; 9, present work
4658	Unidentified coincidences	14
4727	3 _{1 3} , 5 _{2 4} , 10 _{1 9}	9, present work
4765	3 _{1 3}	9, present work
4880	4 _{3 1} , 10 _{3 7} ; 8 _{4 4} , 9 _{4 6} ; 10 _{0 10} , 13 _{1 13}	18, 27; 22; 20
4965	4 _{2 2} ; 5 _{1 5} ; 15 _{4 12} ; 11 _{5 7}	18; 19; 29; 9, present work
	16 _{4 12} , 13 _{4 10} , 15 _{1 15} , 23 _{6 18} , 19 _{4 16} , 20 _{2 18}	21
5017	Unidentified coincidences	14
5145	8 _{7 1} , 11 _{5 7} , 8 _{0 8} , 10 _{4 6} , 3 _{1 3} , 11 _{7 5} , 8 _{4 4} , 8 _{6 2} , 12 _{7 5} , 11 _{6 6} , 18 _{4 14} , 6 _{6 0} , 17 _{7 11} , 7 _{1 7} , 20 _{6 14} , 3 _{1 3} , 8 _{2 6} ; 7 _{1 7} ; 5 _{1 5}	17; 17, 20; 20

3.1. LIF observations

3.1.1. Visible pumping

It is well known that N₂O₄ is transparent in the visible [13] but that NO₂ absorbs each of the visible argon laser lines (step 1) [14, 15]. This latter process leads to a resonant LIF (step 2) and to an LIF continuum (steps 3 and 4) [1]. The resonant fluorescence in NO₂ has already been studied in the literature at high resolution for five of the argon laser lines, and in most cases several NO₂ lines were found to coincide with the laser lines [11, 15 - 25]. We were able to assign some of the absorption lines coincident with two additional laser lines, at 4727 and 4765 Å, and to extend the assignments concerning the previously studied 4579 and 4965 Å argon laser lines. Only the assignment of the lower state rotational levels initially pumped by the laser lines $(J_{K_a K_c})_i$ will actually be useful in the present context. This information is presented in Table 1 for the few newly assigned coincidences and for the numerous coincidences already reported in the literature [11, 15 - 29]. Details of the new assignments and examples of the present experimental results are given in ref. 9.

Despite the extensive work devoted to the study of LIF spectra in the literature and also in the present work, Table 1 is still incomplete. This is particularly obvious for two of the laser lines, at 4658 and 5017 Å, for which no assignment is reported. A study of the fluorescence induced with these laser lines was attempted during the present work and was unsuccessful, probably because of the weakness of the resonant fluorescence lines. Several weak fluorescence lines are still unidentified on the various LIF spectra. Most of them probably result either from unusual selection rules or from collisional processes affecting the upper rovibronic levels [22, 24, 25].

Finally, as another possible fate of the visible excitation, it should also be mentioned that the reaction



can be expected to occur, as shown in ref. 30, where NO_2^* results from the visible excitation (step 1). The production of NO in the present experiments will be discussed in Section 3.3.

3.1.2. UV pumping

The absorption of UV radiation in the $\text{NO}_2\text{-N}_2\text{O}_4$ system has been extensively studied in the literature [31, 32]. UV radiation photodissociates both NO_2 [31] and N_2O_4 [32] via



and



The electronically excited NO_2^* produced in eqn. (5) then decays via



The role of eqns. (5) and (6) was confirmed in our experiments by monitoring the UV LIF. The broad structureless continuum characteristic of NO_2^* was seen to extend throughout the visible.

The formation of NO according to eqn. (4) could also be shown to occur in our cell. The NO detection will be reported in Section 3.3.

3.2. IR absorption coefficients

The IR absorption coefficients for the various CO laser lines in the range 1598 - 1780 cm^{-1} are presented in Fig. 3(a). They can be classified into two groups of strongly absorbed lines: (i) a group below 1659 cm^{-1} , and (ii) a group between 1700 and 1790 cm^{-1} .

As shown in Table 2, the laser lines of the first group coincide, within less than 0.03 cm^{-1} , with the NO_2 absorption lines in the ν_3 fundamental band assigned in the literature [33, 34]. Therefore they correspond to absorptions involving NO_2 in its ground electronic state (step 8). Only the

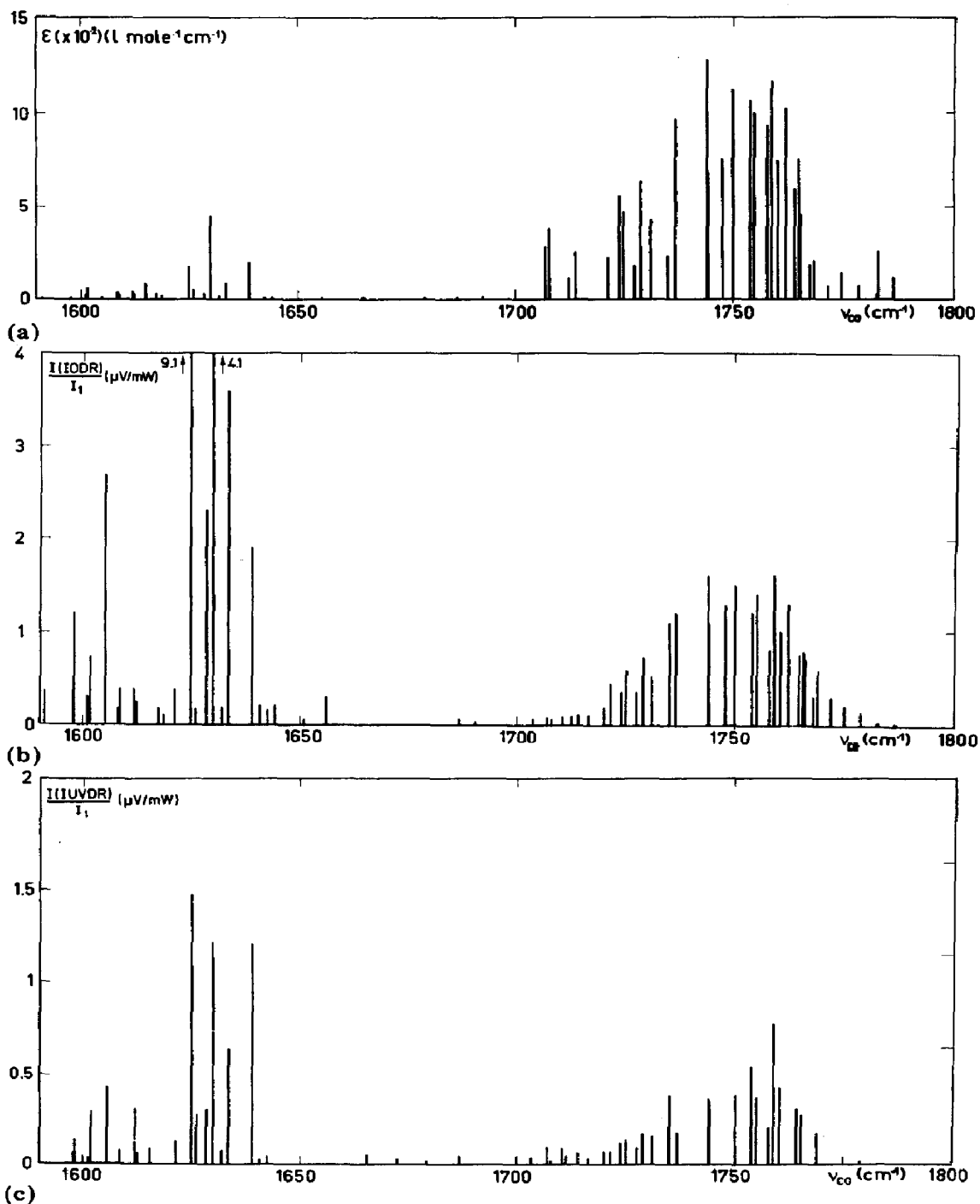


Fig. 3. Signals monitored in $\text{NO}_2\text{-N}_2\text{O}_4$ with the various available $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}$ laser lines in the range $1590 - 1790 \text{ cm}^{-1}$: (a) IR absorption coefficients; (b) IR optical double-resonance signals, normalized for 1 mW IR laser power due to the 4880 \AA argon laser line (7 W); (c) IR optical double-resonance signals, normalized for 1 mW IR laser power, due to the UV laser lines (2.4 W).

TABLE 2

IR transitions in ν_3 , NO_2 , probed with the CO laser lines, and the corresponding absorption coefficients (electron spin assignments are omitted)

CO (cm^{-1}) ^a	NO_2 (cm^{-1}) ^b	Assignment in ν_3 ^{b,c}	ϵ ($1 \text{ mol}^{-1} \text{ cm}^{-1}$)
1597.9357	1597.959	$25_{9,16} - 25_{9,17}$	7 ± 1
1601.6222	1601.613	$14_{3,12} - 15_{3,13}$	62 ± 9
1605.2760	1605.244	$6_{5,2} - 7_{5,3}$	60 ± 9
1624.9200	1624.920	$24_{7,18} - 23_{7,17}$	178 ± 27
1628.4831	1628.482	$29_{7,22} - 28_{7,21}$	30 ± 5
1629.8628	1629.871	$19_{3,16} - 18_{3,15}$	380 ± 57
1633.5188	1633.515	$24_{3,22} - 23_{3,21}$	85 ± 13
1638.9871	1638.989	$29_{1,28} - 28_{1,27}$	204 ± 30

^aSee ref. 8.

^bSee ref. 33.

^cSee refs. 33 and 34.

lines corresponding to the strongest absorption coefficients are considered in Table 2.

The absorption coefficients of the laser lines of the second group make up the shape of a structureless vibrational band centred at $1748 \pm 5 \text{ cm}^{-1}$ with a width of 35 cm^{-1} (full width at half-maximum). These characteristics agree very well with those of the conventional low resolution IR spectrum of the ν_9 fundamental band of N_2O_4 [35]. This set of absorptions can therefore be attributed to N_2O_4 and the IR absorption is represented by step 9.

The CO laser also allows the NO that might be produced in reactions (3) and (4) to be detected. Indeed, there is a known coincidence with the $^{13}\text{C}^{16}\text{O}$ laser line at $1812.6418 \text{ cm}^{-1}$ which is only 27 MHz below the P(17.5) 1-0 $^2\Pi$ transition in NO [36] (step 10).

The role of the CO laser as a probe of NO_2 , N_2O_4 and NO will appear in the next section.

3.3. IODR signals

All CO laser lines in the range 1598 - 1790 cm^{-1} were investigated for each argon line in order to detect possible IODR effects. Two representative sets of IODR results are presented in Fig. 3. They were obtained by coupling each available IR laser line with the 4880 Å laser line on the one hand (Fig. 3(b)) and with the UV laser lines on the other hand (Fig. 3(c)). The values of $I(\text{IODR})/I_1$ ($\mu\text{V mW}^{-1}$), *i.e.* the double-resonance intensity normalized for 1 mW IR power, are presented in Figs. 3(b) and 3(c).

A closer look at the results summarized in Fig. 3 shows that the IODR signals correspond, for each optical pumping, to the same IR laser lines, and that they have similar relative intensities from one optical excitation to another. These comments also apply to the IODR signals observed with the other visible excitations which, however, have weaker intensities than those

observed with the 4880 Å laser line. The IODR signals actually correspond to those IR laser lines which are strongly absorbed in NO₂ or in N₂O₄, as shown by the comparison of Fig. 3(a) with Figs. 3(b) and 3(c). The double-resonance signals thus imply IR absorption in the ground electronic states of either NO₂ or N₂O₄. Their full interpretation will be provided and discussed in the next sections.

We were also able to detect the NO formed in the UV photodissociation of NO₂ (eqn. (4), step 6) by observing an IR UV double resonance (IUVDR) signal at 1812 cm⁻¹ corresponding to IR absorption in NO.

The production of NO with visible excitation, expected from eqn. (3) (step 5), was also looked for with the same procedure. The corresponding IODR signal could only be observed when the detection sensitivity was increased by overlapping rather than by crossing the two laser beams in the cell.

4. Qualitative interpretation of the results

4.1. *Optically-induced perturbations in NO₂*

The observation of a resonant LIF in NO₂, which can be identified in terms of specific absorption-emission schemes, clearly indicates that some particular rotational levels, assigned in Table 1, are affected by the visible pumping. These effects, which we will refer to as quantum effects, are usually also those involved in double-resonance spectroscopy. Generally, in double-resonance spectroscopy the radiation fields are resonant for two transitions of a molecule that either share a common quantum level (three-level scheme) or exhibit some preferred collisional coupling (four-level scheme) [37]. In the present case, a comparison between the assignments of the levels initially pumped by the visible laser lines, given in Table 1, and those involved in the IR probe transitions, given in Table 2, demonstrates the potential existence of a single three-level scheme among all possible combinations. It involves the 7₅₃ level which belongs to two transitions, the IR and visible, which could be simultaneously excited by the 1605.2760 cm⁻¹ and the 4545 Å laser lines. However, the corresponding IODR signal, though intense, did not show any enhancement compared with those obtained with the same IR but different visible excitations. This three-level scheme is therefore probably not responsible for the corresponding observed signal. Moreover, despite the large variety in the levels initially pumped, and assigned in Table 1, the various IODR signals observed in NO₂ show similar relative intensities for each different visible excitation. Four-level schemes, which usually involve preferred collisional couplings, cannot therefore be entirely responsible for the observed IODR signals. It thus appears that under our experimental conditions the optical pumping has a dominant effect which is not a quantum or level-to-level effect but rather a uniform effect dispersed over all the levels. This is confirmed by the double-resonance signals observed with the UV excitation. The UV beam which photodis-

sociates NO_2 (step 6) can only be expected to pump uniformly on the ground state rotational levels. As already pointed out, the results show that the IUVD signals correspond to the same IR laser lines and also show relative intensities similar to those induced by the visible pumping. Therefore the same (uniform) population perturbation results from the UV and visible pumpings. The origin of this perturbation, which we will refer to as a chemical effect, can be understood by considering the IODR signals corresponding to the IR absorption in N_2O_4 .

4.2. *Optically-induced perturbations in N_2O_4*

It has already been pointed out that N_2O_4 is transparent in the visible and it cannot be involved in any of the visible excitations. Only NO_2 can be excited by the visible laser lines. Therefore the IODR signals corresponding to IR absorption in N_2O_4 with visible pumping, *i.e.* the signals observed around 1748 cm^{-1} in Fig. 3(b), constitute a peculiar observation. Those signals do indeed involve pumping in one species, NO_2 , and probing of the other species, N_2O_4 . The two species are only connected by a chemical equilibrium. This equilibrium therefore appears to have a critical role in the response of the system to the optical pumping. As a result of the visible pumping which perturbs the population of specific ground state rotational levels in NO_2 , the concentration of NO_2 in its ground electronic state is affected as a whole. The chemical equilibrium responds to this perturbation and both the NO_2 and the N_2O_4 ground state concentrations are modified. This modification, which affects the population of all the rotational levels, is probed by the CO laser lines and leads to the observation of IODR signals in NO_2 and in N_2O_4 . This interpretation of the double-resonance results implies that the variations in concentration on both sides of the equilibrium are connected because they have the same chemical origin.

We should also comment on the other IODR signals corresponding to IR absorption in N_2O_4 but observed with UV pumping, *i.e.* the signals around 1750 cm^{-1} in Fig. 3(c). According to the data summarized in Fig. 2, both NO_2 and N_2O_4 absorb the UV radiation (steps 6 and 7). The concentration of N_2O_4 is then affected not only by the indirect response of the chemical equilibrium, but also by the direct pumping in N_2O_4 . This scheme is more complex to interpret than that with the visible pumping. It will nevertheless be considered quantitatively in the next section.

5. Quantitative interpretation of the results

5.1. *Efficiency of the optical pumping*

There appears to be a specific relation between the normalized double-resonance intensities $I(\text{IODR})/I_1$ and the IR absorption coefficients ϵ . This dependence is displayed in Fig. 4 for each of the two groups of signals occurring with 4880 \AA excitation (Figs. 4(a) and 4(b)) and with UV excitation (Figs. 4(c) and 4(d)). Only the strongest IODR signals corresponding to IR

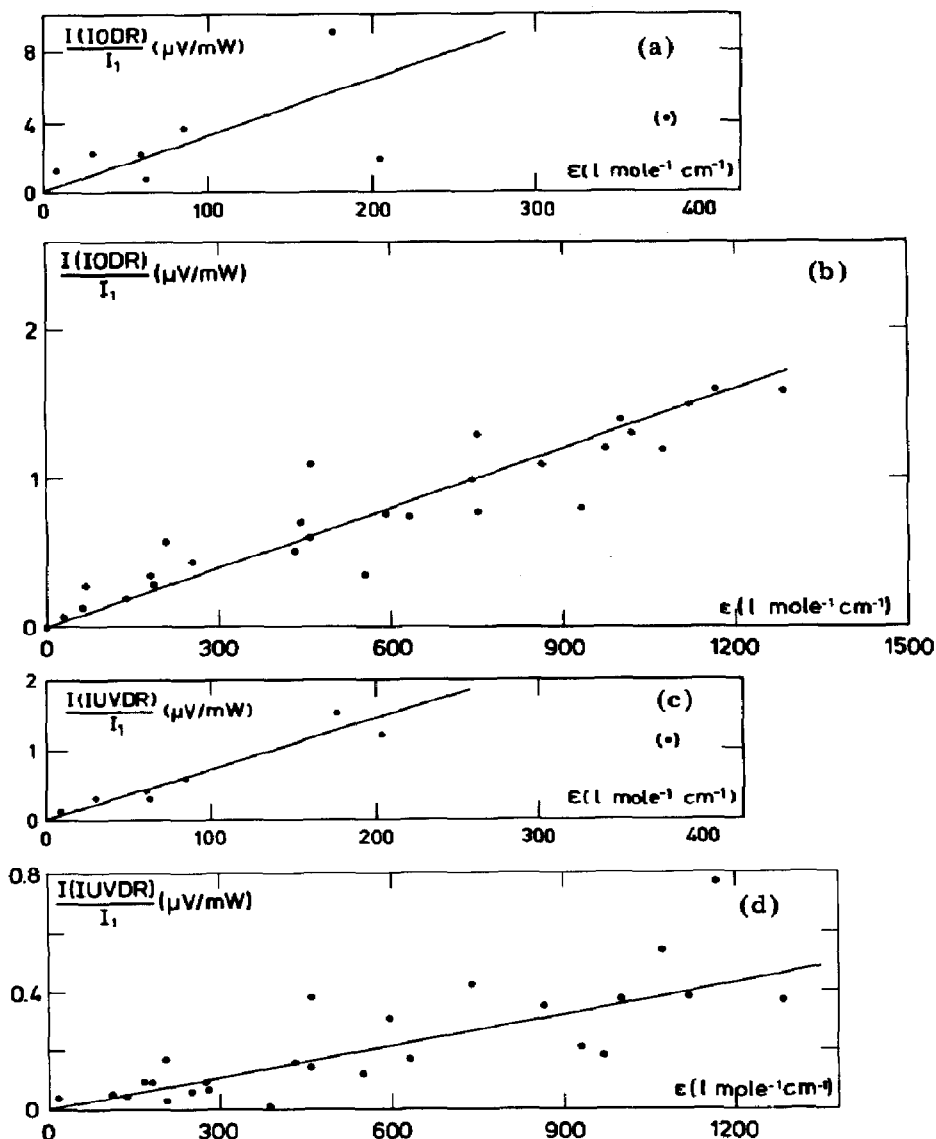


Fig. 4. Correlation between the intensity of the IR optical double-resonance signals observed in NO_2 - N_2O_4 , normalized for 1 mW IR laser power, and the absorption coefficient of the corresponding IR laser lines, in the case of excitation with the 4880 Å argon laser line (7 W), with (a) IR absorption in NO_2 and (b) IR absorption in N_2O_4 ; and in the case of excitation with the UV argon laser lines (2.4 W), with (c) IR absorption in NO_2 and (d) IR absorption in N_2O_4 .

absorption in NO_2 are taken into account in Figs. 4(a) and 4(c). For each group the plots in Fig. 4 demonstrate a linear relationship between the two quantities, which can be understood by analysing the mechanism of the double-resonance detection.

The absorption of the IR beam by NO_2 or N_2O_4 in the interaction volume can be described by the Beer-Lambert law

TABLE 3

Comparison between the variations in concentration Δc (mol l^{-1}) induced in NO_2 and in N_2O_4 by the optical pumping due to argon laser lines

Optical pumping	$\Delta c(\text{NO}_2)$	$\Delta c(\text{N}_2\text{O}_4)$
4880 Å ^a	1.2×10^{-6}	3.8×10^{-8}
UV ^b	1.4×10^{-6}	7.3×10^{-8}

^aLaser power, 7 W; length l of the interaction volume, 0.5 cm; chopping frequency, 713 Hz.

^bLaser power, 2.4 W; length l of the interaction volume, 0.07 cm; chopping frequency, 375 Hz.

$$I_1 = I_0 \exp(-\epsilon c_1 l) \quad (7)$$

with c_1 the concentration of the absorbing species and $l = 0.5$ cm and $l = 0.07$ cm for the visible and UV excitations respectively. The absorption coefficients for the various probe laser lines have already been presented (see Table 2 and Fig. 3(a)).

The chopped optical pumping leads to a modulated variation (Δc) in the concentration of NO_2 and N_2O_4 . Therefore, in the presence of the two laser beams, the IR absorption is described by

$$I_2 = I_0 \exp(-\epsilon c_2 l) \quad (8)$$

with $c_1 - c_2 = \Delta c$.

Combining eqns. (7) and (8) gives

$$I_2 = I_1 \exp(\epsilon \Delta c l) \quad (9)$$

The difference, $\Delta I = I_2 - I_1$, which is too small to be determined by direct reading of I_2 and I_1 on the IR power meter, gives rise to the double-resonance signal. Assuming that $\epsilon \Delta c l \ll 1$, then for each IODR signal

$$I(\text{IODR}) = \alpha(I_2 - I_1) \quad (10)$$

or

$$I(\text{IODR}) = \alpha I_1 \epsilon \Delta c l \quad (11)$$

and

$$\frac{I(\text{IODR})}{I_1} = \alpha(l \Delta c) \epsilon \quad (12)$$

where α is a proportionality factor which is included because the units of $I(\text{IODR})$, measured in microvolts, and those of I_1 and I_2 , measured in milliwatts, are different.

This simple model appears to fit the experimental results presented in Fig. 4. The linear relationship between the two quantities $I(\text{IODR})/I_1$ and e

is, according to eqn. (12), a clear indication that Δc has a constant value in each group. For each case, Δc can be calculated from the data represented in Fig. 4. The conversion factor α , needed to obtain such values from those of $I(\text{IODR})/I_1$ measured in microvolts per milliwatt, has been determined by comparing the intensity of IR laser lines, measured with the lock-in amplifier, and their power, measured with the power meter. This factor is $I(V)/I(W) = 70$. The results are presented in Table 3. These effects are compared in the next section.

It should be mentioned that the normalized signal $I(\text{IODR})/I_1$ corresponding to the strongest IR absorption coefficient in NO_2 , *i.e.* the point between parentheses in Figs. 4(a) and 4(c), was not considered in the calculation of Δc because the associated experimental value of I_1 was extremely low and therefore very uncertain.

It therefore seems possible to use the experimental results to quantify the effect of the optical pumping on the concentrations of NO_2 and N_2O_4 .

5.2. Role of the chemical response

The observation of a double-resonance signal when probing NO_2 and N_2O_4 is a clear indication that both sides of the equilibrium are affected by the optical pumping. The quantitative treatment of the results, in terms of the amount of each species perturbed by the pumping, demonstrates that this amount, given in Table 3, is the same for both species. Indeed, it appears to be of the order of 1% of the initial concentration for both species. This behaviour is observed when the initial excitation is restricted to one chemical species (visible laser pumping in NO_2 only), and also when the excitation affects directly both species (UV laser pumping in NO_2 and N_2O_4). Therefore the quantitative information deduced from our results definitively confirms the existence of a balanced chemical response of the system to the optical perturbation.

Unfortunately, the values of the quantities Δc given in Table 3 are small so that a closer comparison between them appears meaningless because of the accuracy to which the other relevant quantities, such as the equilibrium constant and the initial pressure, are either known or measured.

6. Discussion

Compared with our previous preliminary studies [9, 12] of the NO_2 - N_2O_4 chemical system, the present work contributes three main items of information which need to be emphasized as they open new areas of discussion.

(a) It brings together the dynamic and spectroscopic observations concerning the effects of Ar^+ laser pumping in NO_2 - N_2O_4 . These observations demonstrate the occurrence of both quantum and chemical effects in the same system, giving new insight into the NO_2 problem. The relative importance of each of these effects will be discussed in this section.

(b) IODR observations are reported not only with optical excitation in NO_2 and IR monitoring in N_2O_4 , as in ref. 12, but also with IR monitoring in NO_2 itself. Quantitative information could therefore be obtained concerning the response of the species to the optical perturbation on both sides of the equilibrium, allowing the role of the equilibrium to be demonstrated. This new development was presented in Section 5 and it will be discussed further here.

(c) Double-resonance signals are reported for the first time with UV excitation. The results are therefore extended not only to NO_2 with optical excitation but also to NO_2 and N_2O_4 with UV excitation. A comprehensive discussion of the various sets of double-resonance results will be provided in order to suggest possible kinetic mechanisms responsible for the observations and to point out their expected relative importance.

6.1. Quantum and chemical effects

The absence of quantum effects among the double-resonance signals, *i.e.* the absence of three- or four-level schemes, needs to be discussed. Indeed, quantum effects were demonstrated with the LIF experiments which were performed under experimental conditions similar to those of the double-resonance experiments, and such effects could also be expected to contribute to the double-resonance intensities. A unique three-level scheme was pointed out in Section 4.1. from the known assignments of the visible and IR coincidences. The absence of a corresponding strong IODR signal can probably be attributed to the poor efficiency of the optical coincidence with the 4545 Å laser line mentioned in the literature [23]. As pointed out previously, the double-resonance results did not show any stronger evidence for preferred collisional coupling schemes. However, it should be noted that the signals observed in NO_2 with UV pumping (Fig. 4(c)) present a better-defined relationship with the ϵ values than in the case of visible excitation (Fig. 4(a)). The Δc values, given in Table 3, are also much more comparable in the case of UV pumping. A possible explanation is that some of the IODR signals observed in NO_2 with the visible pumping would include a weak but significant contribution from the usual four-level schemes. This contribution, which differs from one signal to another, might explain the poor relationship observed with visible excitation.

The IODR signals reported here were observed at various pressures between 1 and 20 Torr as mentioned in Section 2. The results show that there is a linear dependence of the IODR intensity on the partial pressure of the corresponding chemical species, *i.e.* the species absorbing the IR radiation. Extrapolation of these results indicates that the chemically induced double-resonance signals would be extremely weak at low pressures. Other microwave optical and microwave IR double-resonance studies of NO_2 described in the literature [26 - 29] were all performed at low pressures, typically 100 mTorr. It is therefore very unlikely that these other double-resonance signals, attributed to quantum effects, could include a significant contribution from the chemical effect reported here.

Another (IR optical) double-resonance study of NO_2 should be mentioned specifically. IODR signals were observed in that study using the visible argon laser lines and attributed to non-identified coupling schemes in NO_2 [38]. The experimental observations reported in that study have several features similar to those discussed in this paper. However, the interpretations of the two sets of results can hardly be compared directly. In the previous case a high power IR laser was used. It was, moreover, a CO_2 laser, whose lines in the $10\ \mu\text{m}$ range do not correspond to any ground state absorption, and could only be absorbed between excited vibronic levels. Thus the present study appears to be different in the sense that the IR laser lines, in our case, have a probe role and concern the molecules in their ground electronic states.

The present double-resonance mechanism, based on a chemical equilibrium connecting two species, appears to be an original scheme. It can be compared with another peculiar scheme discussed in the literature [39] which involves a physical rather than a chemical effect. In that case, a microwave beam pumps a molecule placed in the cavity of an IR CO_2 laser on a specific transition. The resulting saturation effect changes the characteristics of the gas and therefore the output power of the IR laser, although the laser line is off resonant. Both the physical and the present chemical mechanisms are indirect and have the advantage of being less restrictive than the usual quantum schemes. However, because of the lack of specificity, some of the advantages of the double-resonance technique, such as help in the assignment, are lost.

6.2. Kinetic mechanisms

The absence of signed quantities among the present results is apparent. The values of Δc given in Table 3 are actually absolute variations and their relative sign may be extracted from the experimental measurements concerning the phase associated with the IODR signals, which have not yet been mentioned. A 0° and 180° phase shift is expected for signals which characterize similarly and oppositely varying quantities respectively. In the present case, the phases associated with the signals corresponding to IR absorption in NO_2 or N_2O_4 , coherent within each group of signals, appeared shifted by 130° for the visible excitation and by 110° for UV excitation. The discrepancy with the expected behaviour probably indicates that several mechanisms with different delays are induced by the chopped optical pumping. Each of these mechanisms must contribute to the phase and also to the intensity of the observed IODR signals. We will discuss briefly the kinetic aspect of some of the steps presented in Fig. 2 and point out, if possible, their expected relative importance.

6.2.1. Formation of NO

The NO_2 - N_2O_4 chemical system presented in Fig. 2 is a closed system except for the formation of NO (steps 5 and 6) which introduces a leak, *i.e.* which decreases the concentration of the starting species NO_2 and N_2O_4 . The

importance of that leak is reduced significantly by the flow conditions used in the experiments. The intensities of the perturbations induced by the UV and visible beams should be compared in order to determine the importance of NO formation in the system shown in Fig. 2. Indeed, the efficiency of NO formation, as confirmed by the observations reported in Section 3.3, is much larger with the UV excitation which directly photodissociates NO_2 with a quantum yield of unity [31], and the perturbation, *i.e.* the corresponding Δc value, must also be larger if that step has a predominant role. The visible and UV Δc values, given in Table 3, are unfortunately not directly comparable because they are derived under different experimental conditions, such as the laser power, the laser beam diameter and the chopping frequency. An estimation of the influence of these experimental factors seems to indicate that the intensity of the perturbation is similar for the UV and visible excitations. We therefore do not believe that the formation of NO contributes significantly to the mechanisms responsible for the observed IODR signals.

6.2.2. Removal of NO_2

The absorption of the visible beam leads to a direct decrease in the ground state population of NO_2 . The response of the equilibrium to the perturbation is expected to be instantaneous [40]. A corresponding simultaneous decrease in the N_2O_4 concentration must therefore result from the visible excitation. This mechanism is probably one of the key mechanisms responsible for the chemical perturbation. A similar removal of NO_2 exists in the case of the UV pumping, which probably also contributes predominantly to the intensity of the IUVDR signals. As pointed out previously, the mechanism is, however, more complex to interpret in that case because of the UV absorption in both the species NO_2 and N_2O_4 .

6.2.3. Thermal effect

The importance of the thermal response of a chemical equilibrium to an optical perturbation in a closed system has been stressed in the literature [5]. The NO_2 - N_2O_4 system was actually studied in that particular context, using the visible argon laser lines to heat up the system. However, the role of the thermal effect appeared not to be definitively demonstrated in that study. Such a thermal process, expected to be slow compared with the chopping frequency, would lead, unlike the removal of NO_2 , to an increase in the NO_2 ground state concentration at the expense of the N_2O_4 concentration.

In order to understand fully the IODR observations, both the excitation step, *i.e.* the direct removal of NO_2 (steps 1 or 6) and the thermal effect may have to be taken into account. These effects, both modulated at the chopping frequency, are characterized by different delay times because of

the slower response of the thermal effect. They both contribute to the decrease in the concentration of N_2O_4 but have the opposite influence on the concentration of NO_2 . The resulting time-modulated variation in the concentration of the two species might well present phase and amplitude characteristics which could fit the present observations. The study of such a kinetic model appears to be beyond the scope of the present paper, which is limited to the spectroscopic interpretation of the results.

7. Conclusion

In the present study, the $NO_2-N_2O_4$ chemical system was perturbed by an optical pumping affecting directly either NO_2 alone, with a visible argon laser beam, or both NO_2 and N_2O_4 , with a UV argon laser beam. The effects of the optical pumping on the molecules in their ground electronic states were studied through the characteristics of the resonant LIF. They were also monitored in separate IODR experiments, with the help of an IR CO laser probing specifically NO_2 , N_2O_4 and NO in their ground electronic states. The results, in combination with literature data, demonstrate that the optical pumping leads to quantum and chemical perturbations in the system. The quantum or microscopic perturbations, assigned using the LIF technique, involve the populations on specific rotational levels in NO_2 , which are pumped with the visible laser beam. The chemical or macroscopic effect, monitored with the IODR technique, concerns the concentrations of the two species which are modified by the response of the chemical equilibrium to the optical perturbation. A model describing the efficiency of the macroscopic perturbation in terms of the Beer-Lambert law was applied to the IODR results. It enabled the role of the chemical equilibrium on the response of the system to be demonstrated.

The results therefore indicate that the optical pumping leads, in addition to the expected microscopic effects, to a real macroscopic transition, *i.e.* brings the system to a new steady state. This macroscopic transition is controlled by a chemical response of the system which re-equilibrates the concentrations of NO_2 and N_2O_4 perturbed by the optical pumping. This effect affects the population of all rotational levels in NO_2 in its ground state and must therefore contribute to any light-induced process in that molecule. This contribution is, however, expected to be very weak under low pressure conditions.

The characteristics (amplitude and phase) of the observed IODR signals certainly reflect the kinetic schemes which are induced by the optical pumping. It is our hope to understand better those schemes which, in addition to absorption, emission and photodissociation processes, must include the chemical equilibrium relation and possibly a thermal response of this chemical equilibrium.

The use of the IR optical double-resonance technique in the present dynamic context provides further scope for this spectroscopic technique. It could indeed be applied to the study of chemical species connected not only

by a chemical equilibrium but also by an isomerization process or by a weak intermolecular bonding force, such as that encountered in van der Waals molecules, and it could provide new structural, spectroscopic, kinetic or thermodynamic information about such chemical systems.

Acknowledgments

We wish to thank Professor G. W. Hills (Bell Lab., Allentown, U.S.A.) for his help during the first development of this work. We also warmly thank Professor R. Colin, Professor G. Nicolis, Dr. G. De Maré, Dr. M. Godefroid, Dr. P. Mandel, Dr. J. Olbregts (ULB, Belgium), Professor Rosenblatt (Berkeley, U.S.A.) and Dr. J. K. G. Watson (HIA, Canada) for stimulating discussions and/or their critical reading of the manuscript.

Financial support from a NATO travel grant (035/83) and from operating grants from the SPPS (Contract ARC No. 17) and the Fonds National de la Recherche Scientifique (FRFC No. 2.45582) is acknowledged.

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