NO(X,v) DISTRIBUTIONS IN RF DISCHARGES: CONDITIONS FOR A VERY HIGH VIBRATIONAL PUMPING

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Abstract

NO first overtone IR emission spectroscopy measurements in a rf discharge are presented, in which the emission from high vibrational levels, up to v=22, is clearly observable.

Introduction

The conditions for achieving and detecting a high vibrational excitation of NO ground state molecules in a rf electrical discharge have been investigated. The present work is motivated by the low number of measurements concerning the excitation of vibrational levels higher than 16. This lack contrasts with the wide interest of this molecule in various fields, such as the upper atmosphere chemistry, space shuttle re-entry problems, de-pollution of the atmosphere, CO_2 laser kinetics etc. The knowledge of the main rate coefficients responsible of the vibrational pumping is poor. The prevalent opinion is that the vibrational excitation is severely limited by depopulation channels that are opened when the excitation reaches the levels v>16. The pre-eminent channels are supposed to be dissociation, electronic excitation [1], and strong V-T relaxation [2]. Very recently an experiment based on selective vibrational pumping of NO isolated in Argon matrix by IR laser [3] revealed the capability of NO to reach vibrational excitation up to v=27 by V-V transfer, before electronic excitation occurs.

In our previous investigation [4] we were able to observe first overtone radiation from levels up to v=17, generated by an external electrodes rf discharge in a He-NO mixture. The v=17 limit was not, however, intrinsic to the vibrational excitation, but had instrumental origins. First of all, the In-Sb detector was equipped with a 1.4 - 3.5 μ m bandpass cold filter that improved the D* but stopped radiation from v>17 levels. Moreover blackbody radiation from the surroundings, especially from the discharge walls, starts to be intolerably high at wavelengths higher than 3.2- 3.3 μm, due to the very low NO infrared emission, so that its subtraction becomes more and more aleatory

when dealing with higher vibrational levels. In the present work we have dropped these two difficulties, by removing the cold filter and by pulsing the discharge at a 4 msec period. The lock-in detection synchronised to the discharge pulse then reveals only discharge generated emissions, and rejects the continuos environmental background. By virtue of such improvements, we have been able to observe up to level v=22 emission. The conditions for such high excitation will be discussed. We will also discuss briefly an attempt of cooling the gas mixture in order to observe effects of the gas temperature on the vibrational distribution.

Experimental apparatus and calculus

A scheme of the experimental apparatus is shown in fig. 1. The discharge is operated in a 4 cm internal diameter pyrex tube by a three annular electrodes structure, with the middle electrode connected to the 13.56 MHz rf power supply. The length of the glow region is about 30 cm. A square TTL pulse generator, with 4 ms period, triggers the discharge supply and, at the same time, provides the synchronising signal to the lock-in amplifier. By this way, only emissions produced by the discharge , and therefore modulated by the discharge pulse, are measured.

The NO first overtone infrared emission along the axis of the discharge tube is detected by an optical arrangement composed of a 0.5 m monochromator, equipped with a 300 grooves/mm grating blazed at 3 μm, and a LN_2 cooled In-Sb detector. A collimating lens focuses the radiation into the entrance slit. The input and output slits are opened at their maximum width, 3 mm, due to the low infrared intensity. A 2.3 μm low-pass filter stops higher order radiation up to 4.6 μm. A dry nitrogen flux purges the whole optical path from water vapour, and the calibration of the apparatus optical

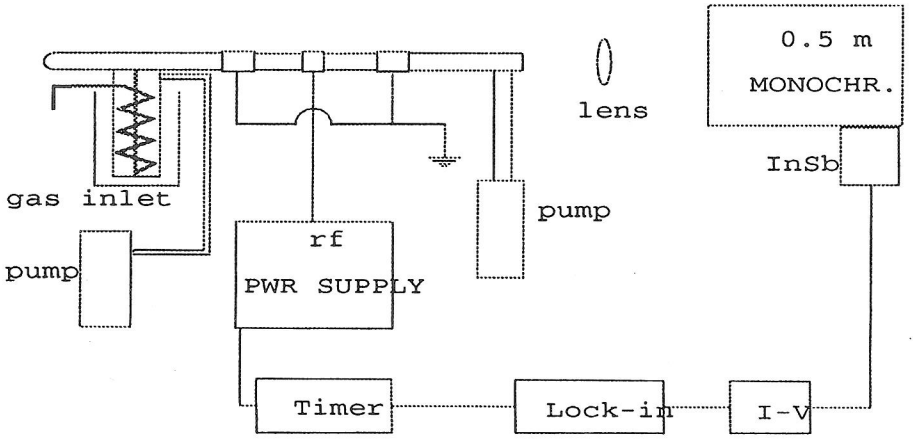
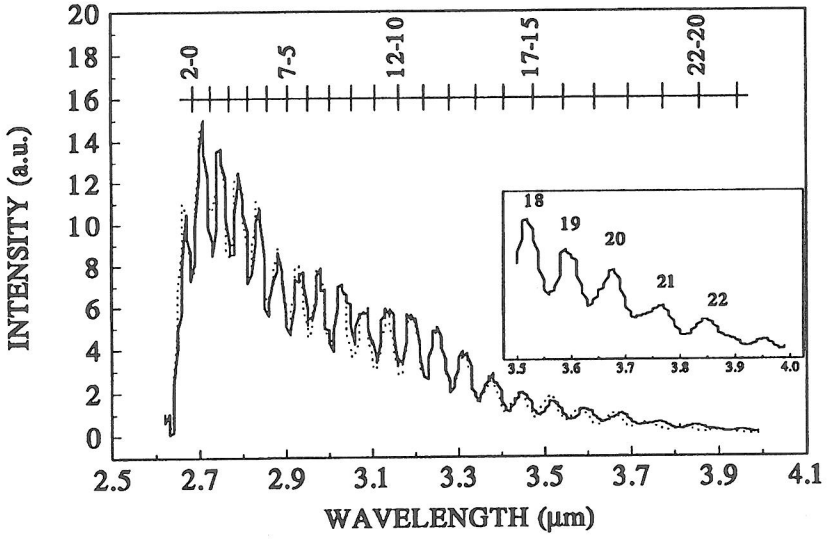


Fig. 1 Scheme of the experimental apparatus

response is achieved by a standard silicon carbide infrared source.

A device for pre-cooling the gas mixture is provided. The gas flows through a coil that is separated from a liquid nitrogen bath by a cavity filled with He at an adjustable pressure. The variation of He pressure modifies the thermal exchange and then the temperature of the flowing gas at the exit of the coil.

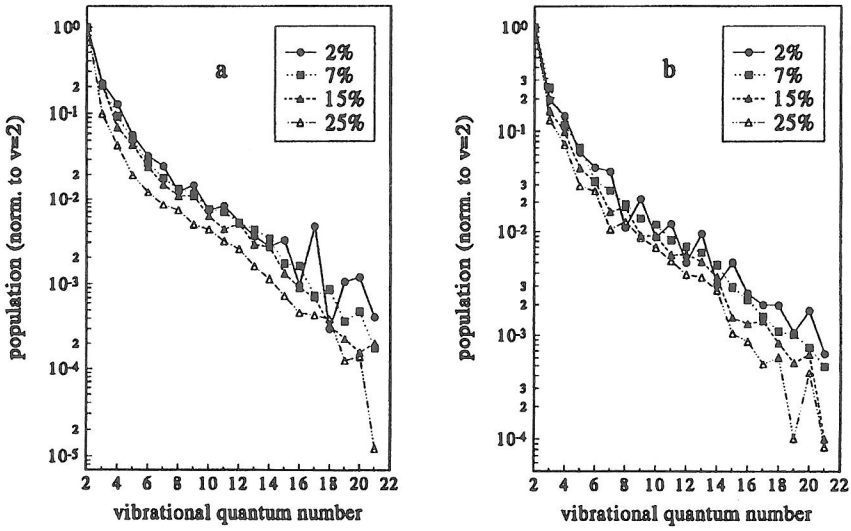
A synthetic spectrum is calculated according to the constants given in [5] and the transition probabilities of [6]. The calculation takes into account the P, Q and R branches of the two sub-states $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ of NO(X) and the monochromator instrumental function. The vibrational distribution for $v \geq 2$ is calculated as the set of populations that minimises the mean square error of the emission intensities in the positions of the maxima of the spectrum. The rotational temperature is left as a parameter that is adjusted in order to get a good agreement between the calculated and experimental spectra. An example of such comparison is shown in fig 2.



•Fig. 2 Experimental (solid line) and synthetic (dotted line) spectrum at 3.2 Torr, He+10% NO, 2000 sccm flux, 5 w rf power. The rotational temperature is 300 °K. The plot of the highest v bands is expanded for better observation. The band origins are reported on top of the graph

Conditions for high vibrational excitation

To achieve a high vibrational excitation of NO(X) in our discharge apparatus we remind that: a) - the global vibrational excitation obviously increases with increasing discharge power and the infrared emission is proportional to the NO density, but b) - NO is a strong V-T quencher; and c) - increasing the rf power produces more NO dissociation and causes the appearance in the NO first overtone spectral region of He lines and of emissions due to the presence of O_2 in the discharge. The spectrum shown in fig. 2 has been measured at 5 W rf power, 3.2 total pressure of He + 10% NO, 2000 sccm total flux. In such condition we have a well pumped vibrational distribution, up to v=22 (perhaps also v=23 is visible), with the highest infrared intensity, and a spectrum reasonably free of "spurious" emissions. The range of *good* conditions is roughly marked by the colour of the discharge, that is pale green and blue-violet near the sheaths, i.e. the typical colour of a NO discharge. On increasing the rf power, the colour gradually turns to the orange-pink characteristic of He emissions, while downstream an intense green luminescence coming from the recombination continuum appears. The effect of NO addition is clearly observable in fig. 3, where the vibrational distributions, calculated as explained above, show increasing depletion of vibrational levels when more NO is added to the mixture, probably due to both increased V-T relaxation and decreased electron impact pumping.

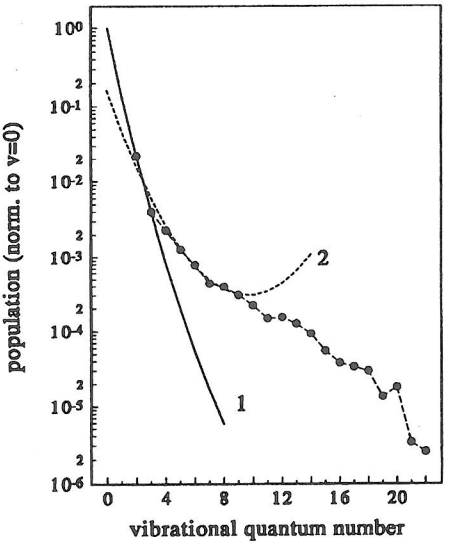


•Fig.3 Vibrational distribution at different NO mixture content, 2000 sccm total flux, 5 W rf power and a) 5.6 Torr, b) 3.2 Torr total pressure.

Results

The distributions shown in fig. 3 suffer the presence of a distortion, especially at low v, due to spatial inhomogeneities of the emitting volume that is roughly entirely collected by the optical arrangement [7]. A distinctive feature of such occurrence is the impossibility of fitting the low v levels population by a Treanor distribution, as shown in fig. 4 for one of our cases. One of the most unfortunate consequence of this problem is the difficulty of determining the rotational temperature with sufficient accuracy from the fitting of the low v part by the synthetic spectrum. In particular the fitting of the 2-0 R branch, that is free from overlaps with branches of the next v, requires a substantially lower rotational temperature, but appears to be quite incompatible with the fitting of the next bands. As a result an incertitude as high as 50 °K affects this determination, with observable consequences on the vibrational population of the low v levels itself. The higher levels are, instead, much less sensitive to this aspect.

Another peculiarity of these results is linked to the temporal variations of the IR signal. Scaling the results of [8], where a temporal analysis of the rise and fall times of the vibrational excitation of levels up to v=12 was made, we observe that in most of our conditions the 2 msec discharge pulse should be sufficiently long to allow reaching a steady state for the vibrational distribution. On the other hand, measurements at longer discharge pulses do not show appreciable variations of the emission spectrum. One must also consider the repetitive nature of the pulse that is superimposed on a roughly 30 msec residence time in the discharge region. It was also shown in [8] that the rise time of the vibrational excitation increases with increasing v, due to the time required by V-V pumping, while the fall time decreases with increasing v, due to the augmented quenching of higher vibrational levels. This very likely implies that the mean amplitude of the IR signal oscillations, that is the quantity measured by the lock-in amplifier, underestimates the shorter oscillations coming from



•Fig. 4 Vibrational distributions in the conditions of fig. 2 and attempts to fit the low v region by a Treanor distribution, 1) - fit with v=2,3, θ_1 = 1340 °K ; 2) fit with v=2,3,4, θ_1 = 2200 °K.

higher v levels. This leads to a possible underestimation of the vibrational population that is progressively higher as v increases (providing the mechanism for high v pumping is purely V-V as in [8]).

The attempts to observe variations in the vibrational distribution produced by a lower gas temperature did not give clear results. We do not observe variations higher than the experimental uncertainty in the spectra measured when the input gas is cooled. However the gas certainly warms up flowing through the 30 cm of the discharge, and, although there are qualitative indications that we could have obtained an *average* cooling of few tens of °K in the whole discharge volume, we have not been able to quantify it owing to the difficulties in determining the rotational temperature mentioned above. We then believe to have qualitative indications that there is a weak temperature dependence of the V-T relaxation rate for all the vibrational levels observed, roughly in the range 250 - 300 °K. This would be in agreement with the results of [9] for v=1, and with some preliminary calculations by Cacciatore. A quantification of such observations is anyway impossible at this stage. We point out, nevertheless, that the gas cooling device is not very effective, especially due to the large discharge volume that, on the other hand, is necessary for having at disposal sufficient IR signal.

We conclude that the vibrational distribution results reported here must be considered as semi-quantitative, and that the most important result is the unambiguous observation of a considerable population of levels up to v=22, and a markedly non-Boltzmann distribution. Such a large vibrational excitation is comparable to that observed in solid matrix experiments [3], and opens the way for V-E processes to be operative.

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