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RYDBERG STATES AND INTRAMOLECULAR RELAXATION OF NO TRAPPED IN RARE GAS MATRICES

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#### ABSTRACT

Three new progressions consisting of broad bands have been observed in the absorption spectrum of NO in solid argon. They are identified as the molecular Rydberg A  $2^2\Sigma^+$ , C  $2^2\Pi$  and D  $2^2\Sigma^+$ -X  $2^2\Pi$  ( $v',0$ ) transitions, blue shifted with respect to the gas phase by  $\sim 0.85$  eV. Excitation of the molecule yields emission from A  $2^2\Sigma^+$  ( $v=0$ ) with large absorption-emission Stokes shifts, and from the valence B  $2^2\Pi$  ( $v=0$ ) and a  $4^2\Pi$  ( $v=0$ ) states. Intensity ratios between these states in Ar, Kr and Xe matrices are given and discussed.

#### INTRODUCTION

Excitation of NO trapped in rare gas matrices by various light sources (refs 1-3) shows that emission stems essentially from the lowest two valence states B  $2^2\Pi$  ( $v=0$ ) and a  $4^2\Pi$  ( $v=0$ ), with a weak contribution from the lowest Rydberg A  $2^2\Sigma^+$  ( $v=0$ ) state. These results suggested that intramolecular relaxation in matrix-isolated NO is a fast process. The observation of Rydberg fluorescence (ref. 3) stimulated the debate concerning the fate of Rydberg states in condensed matter. In effect, Roncin et al. (refs 4,5) noted a disappearance of the rich Rydberg spectrum of NO by trapping it in rare gas matrices. It was argued that the strong interaction of Rydberg orbitals with matrix atoms broadens the bands so strongly that they would merge into the continuum of the light source and be lost in the absorption spectrum. A preliminary experiment using synchrotron radiation indicated a contribution of Rydberg states to relaxation processes (ref.6). Few instances of molecular Rydberg absorption in matrices were reported in the literature and they have been predominantly limited to the first Rydberg excitation. Higher excitations have been reported only for C<sub>2</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>6</sub> and CH<sub>3</sub>I (ref.7) and they were interpreted within the framework of the Wannier exciton model which was successful in explaining the electronic excitations in rare gas solids. Wannier excitons have no parentage with the free species excited states. Using synchrotron radiation at HASYLAB/DESY on the SUPERLUMI set-up (ref.8), we have observed Rydberg states of NO trapped in rare gas matrices which bear direct parentage with the free molecule states. In the first part of this contribution, we will discuss

features of Rydberg absorption and fluorescence, in the second part we will give results concerning intramolecular relaxation within the low lying states of the molecule.

#### RYDBERG SPECTROSCOPY

In Fig. 1 we present an excitation spectrum of the valence M band a(0,7) at 3941 Å of 0.3 % NO/Ar. The spectrum consists of sharp bands previously identified as the B  $2^2\Pi$  - X  $2^2\Pi$  and B'  $2^2\Delta$  - X  $2^2\Pi$  ( $v',0$ ) valence progressions (refs 4,5). They are superimposed on broad shaded bands (FWHM  $\approx 130$  meV) which can be grouped into three different vibrational progressions. It is generally accepted to describe atomic and molecular Rydberg transitions in condensed matter in terms of Wannier excitons (ref.7). Wannier excitons are bound electron-hole pairs described by the hydrogenic formula :

$$E_n^i = E_G^i - \frac{B^i}{n^2}$$

where  $E_G^i$  is the impurity ionization potential in the solid and  $B^i$  an effective Rydberg constant which takes account of the crystal dielectric properties.

Attempts to interpret the broad bands in terms of Wannier series failed for the following reasons :

- No fit, even approximate, of the Wannier formula was possible.
- The intensity  $n^{-3}$  dependance, expected for a hydrogenic series, is not observed for the broad bands (see Fig. 1).
- There are only three progressions and despite a careful search no higher lying progressions or bands were observed.

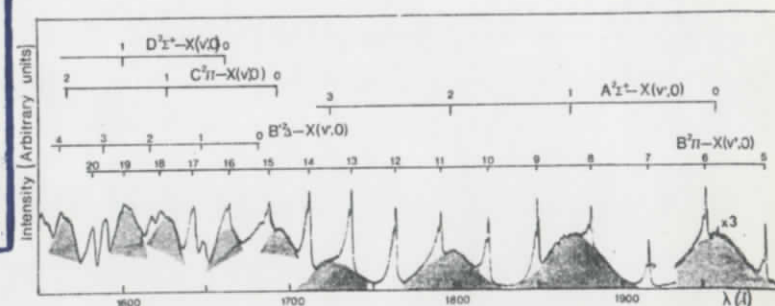


Fig. 1: Excitation spectrum of the M band a(0,7) at 3941 Å of 0.3% NO in solid argon. The Rydberg bands are shown by shaded areas.

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The failure of the Wannier model suggests an interpretation in terms of molecular Rydberg states. The energy spacing between the first four bands is similar to that of the NO Rydberg states (ref.9) and their intensity distribution reproduces that given by Franck Condon factors (ref.10). We assigned them to the lowest  $A^2\Sigma^+$  Rydberg state, with a blue matrix shift of  $\sim 0.85$  eV. Using the gas phase splittings  $A(o)-C(o)$  and  $A(o)-D(o)$  between the lowest three Rydberg states, the higher progressions were identified as the  $C^2\Pi$  and  $D^2\Sigma^+ - X^2\Pi(v',o)$  Rydberg transitions in a straightforward manner. The shift of  $0.85$  eV for the NO Rydberg states in argon is of the same order of magnitude as that of the atomic like  $n=1$  exciton in pure and rare gas doped solid argon (ref.11). The cut-off in Rydberg absorption is related to the impurity ionization potential in the solid  $E_G^1$ , given by (refs 7,11):

$$E_G^1 = I_g + P_+ + V_0$$

where  $I_g$  is the gas phase ionization potential,  $P_+$  the medium polarization energy induced by the positive ionic core and  $V_0$  is the free electron energy in the solid. Our calculation gives  $E_G^1 = 8.1$  eV for NO in Ar with the  $V_0$  and  $P_+$  values from ref.11. The highest observed Rydberg state is  $D^2\Sigma^+(v=0)$  at  $7.46$  eV, the next higher state is  $E^2\Sigma^+$  expected to lie at  $8.4$  eV. It appears that the cut-off in Rydberg absorption is due to the large red shift of the ionization limit ( $\sim 1.2$  eV) and the blue shift of the Rydberg states.

Excitation of  $A(v=0)$  yields Rydberg fluorescence bands  $A-X(o,v')$  with  $\text{FWHM} \approx 80$  meV and an absorption-emission Stokes shift for the  $A(o,o)$  band of  $\sim 0.6$  eV (fig.2). These results are explained in terms of microcavity formation where, as a consequence of the repulsive overlap between the extended Rydberg orbital and the matrix atoms, lattice relaxation takes place and a small cavity is formed. This idea of a "bubble", already put forward by Goodman and Brus (ref.3) for NO, is supported by their lifetime measurements which show Rydberg fluorescence decay times close to the gas phase one, it is also discussed for pure solid neon in another contribution to this volume (ref.12). The formation of a "bubble" in equilibrium with its environment takes place by dissipation of phonons (ref.13) and this process is expected to range in the picosecond time scale. Similar features, both static and dynamic, have also been observed for NO in Ne, Kr and Xe matrices. A detailed account of our results will be presented in a forthcoming publication.

#### INTRAMOLECULAR RELAXATION

The excitation spectrum in fig.1 clearly shows participation of Rydberg states in the  $A^4\Pi(v=0)$  valence emission. Similar spectra have been obtained

for the  $\beta(B^2\Pi - X^2\Pi(o,v'))$  bands of NO in Ar and the  $\beta$  and M bands of NO in Kr. Excitation spectra of the  $A^2\Sigma^+(v=0)$  Rydberg emission in Ar and Kr show also the same gross features though with some differences outlined below. On the other hand in Xe, no valence emission whatsoever could be observed, solely  $A(o,v')$  bands appeared.

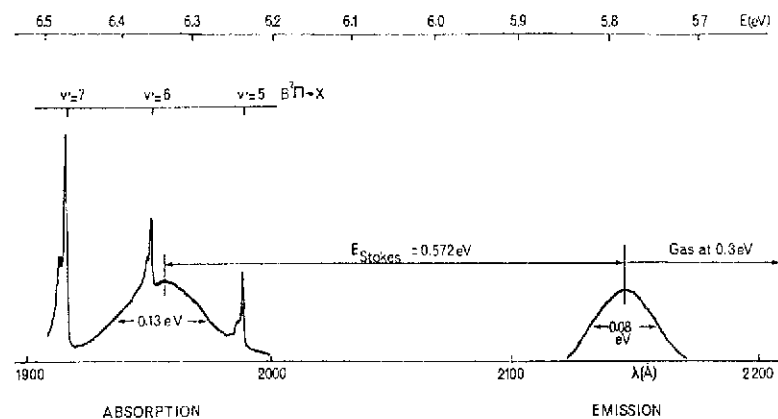


Fig. 2: The Rydberg  $A-X(0,0)$  transition line in absorption and emission shown on the same energy scale. The sharp peaks superimposed on the absorption band are due to valence absorption (see fig. 1).

In fig.3, we present potential curves of the B and a states and of the A state in absorption (upper curve) and emission (lower curve) taking account of the respective matrix shifts in Ar, Kr and Xe. In the following we will present results essentially related to low energy excitation ( $h\nu_{exc} \leq 6.5$  eV), excitation at higher energy complicates the uv emission spectrum by the appearance of new bands of which only one system has so far been identified as the  $L^2\Phi - X^2\Pi$  (ref.14). Our results can be summarized as follows:

- Non-radiative relaxation from Rydberg to valence states are observed in Ar and Kr, and vice-versa only in Ar.
- The emission intensity ratios between the A, B and a states are  $\sim 1:9:90$  in Ar,  $1:1:50$  in Kr and  $1:0:0$  in Xe matrices. The B:a ratios are independent of the excitation energy.
- Relative yields of Rydberg  $A(v=0)$  fluorescence in Ar, Kr and Xe are in the ratio of  $\sim 1:1.5:0.5$ .

The B:a intensity ratios are in fair agreement with previous reports

(refs 1-3). In argon, the B(o) level lies  $\sim 700 \text{ cm}^{-1}$  above the a(7) level and it has been argued (ref. 3) that this large energy gap hinders non radiative dissipation of energy from B(o) to the a state. On the other hand in krypton, B(o) lies  $\sim 70 \text{ cm}^{-1}$  above the a(8) level. This small energy gap might be the reason for the reduced B:a intensity ratio as compared to Ar.

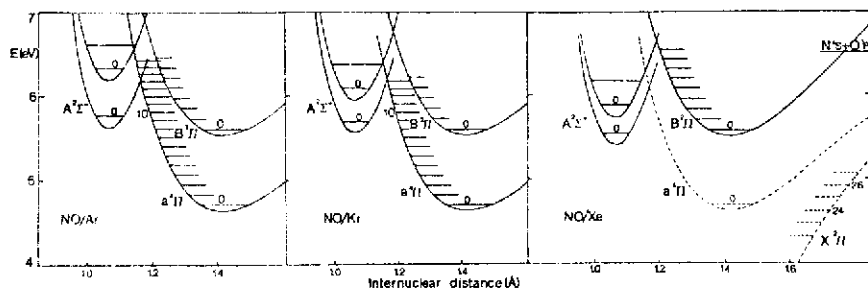


Fig. 3: The potential curves of the lowest three electronic states of NO in Ar, Kr and Xe matrices. The upper curve of the A state is in absorption and the lower one is in emission. For the a state in Xe matrices the gas phase curve (broken line) has been used.

It appears that in Ar and Kr matrices, A(v=0) decays non radiatively to the valence states simultaneous to "bubble" formation. The "bubble" formation lowers the energy of the Rydberg state (fig.3) thus reducing its Franck-Condon overlap with the valence states. Once the bubble formation is completed the Franck-Condon overlap is negligible and the remaining population decays radiatively to the ground state. In Xe matrices, the same process seems to occur but it is possible that efficient non radiative B→a→X relaxation quench valence emission. The yield of A(v=0) emission in Xe would have been expected to be larger than in Ar and Kr as the Franck-Condon overlaps with valence states are smaller (fig.3). It could be that a matrix induced coupling between the A and the B,a states increases the efficiency of the Rydberg to valence non radiative relaxation in Xe matrices.

The Rydberg-valence non radiative processes are complex, "bubble" formation and non radiative transitions are fast processes and it remains to be clarified why it is the latter which predominates in the final population balance, furthermore in Ar matrices back transfers are observed. Finally, the non radiative

transition between Rydberg and valence states is strongly coupled to the lattice since the B-X, and probably the a-X, transitions are weakly coupled (ref. 6) and the A-X transition is strong quadratically coupled to the lattice (ref. 13).

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