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VIBRATIONAL RELAXATION AND ELECTRONIC ENERGY TRANSFER OF N₂ AGGREGATES IN SOLID RARE GAS MATRICES

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Abstract - The vibrational levels \(1\nu'\leq6\) in the \(A^3\Sigma^+\) state of N₂ aggregates have been excited selectively and the population of lower levels has been derived from the intensities in the \(A^3\Sigma^+(\nu')\rightarrow X^1\Sigma^+(\nu'')\) emission spectra. Radiationless relaxation to lower vibrational levels takes place exclusively in steps of \(\Delta\nu'\leq2\) in Xe and Kr matrices. In addition an up conversion in steps of \(\Delta\nu'=3\) is observed. In an Ar matrix steps of \(\Delta\nu'=1\) and \(\Delta\nu'=2\) are superimposed.

I - INTRODUCTION

The \(A^3\Sigma^+\) state of N₂ molecules in rare gas matrices is an exceptional case of slow vibrational relaxation in an excited electronic state in the solid phase. The observations of hot luminescence from the A state after X-ray excitation \(/1, 2/\) have been accomplished recently by investigating luminescence spectra of N₂ in Xe after populating individual vibrational levels of the A state selectively \(/3/\). The bars in the vertical histograms of Fig. 1 represent the population distributions in the vibrational levels of the A state for excitation of the level marked by an arrow \(/3/\). The most important observation in Fig. 1 is that the vibrational quantum number is reduced by two in the first step of relaxation. The increase with N₂ concentration of the extent of relaxation to lower levels indicates that these relaxation processes are due to the interaction between pairs of closely spaced N₂ molecules formed accidently by the statistically distribution of N₂ in the matrix. The experimental population distributions have been described quantitatively by a nonresonant nonradiative energy transfer within N₂ pairs induced by exchange interaction \(/3/\). These experiments demonstrate the possibility to store a selective population of high vibrational levels far from thermal equilibrium for \(10^{-3}s\) and inquire for an application in photochemistry. Furthermore they are a case study for the energy dissipation in aggregates or clusters. In this paper the influence of the matrix on these relaxation processes is investigated experimentally by an extension to Kr and Ar matrices.

Fig. 1 - Experimental population distributions in the vibrational levels of the \(A^3\Sigma^+\) state for two concentrations of N₂ in Xe. The length of the bars in a vertical histogram represents the population; arrow: initially populated level; \(/from\ \text{ref. 3/}\.\)
II - EXPERIMENT

The $1\Sigma^+_g \rightarrow 3\Sigma^+_u$ transition is spin forbidden and has a low transition probability. The spin-selection rule is weakened in matrices of high atomic weight resulting in radiative lifetimes of 0.0015 s, 0.014 s and 0.4 s for the A state in Xe, Kr and Ar matrices respectively /1, 2, 3/. Population of A($v'$) levels by light requires in the case of the lighter rare gas matrices Kr and Ar rather thick samples to compensate for the small absorption coefficient of the diluted N$_2$ molecules. Therefore free standing doped Kr and Ar crystals have been grown from a N$_2$ rare gas mixture with a thickness of 5 mm /4/. The nominal concentrations of 8 atomic % N$_2$ in the Kr and Ar mixtures in the gas handling system are reduced in the crystals according to our experience to about 0.5 - 2 atomic %. The doped crystals have been excited with monochromatized Synchrotron radiation of the Superlumi-beam line at DORIS in Hamburg /5/. The emitted light has been analysed by a vacuum ultraviolet monochromator and an infrared monochromator /6/.

III - EXPERIMENTAL RESULTS

The total emitted light flux detected in zeroth order of the emission monochromator is proportional to the number of photons absorbed in the crystals /3/. Absorption spectra have been taken by monitoring the total emitted light flux and scanning the monochromator for the exciting light. Mean values for the gas to matrix shift of the maxima of the A ($1v'\leq 6$) vibrational bands are given in table 1. Representative line shapes for the X($v''=0$) $\rightarrow$ A ($v'=5$) vibrational bands in Kr and Ar matrix are shown in Fig. 2 on a logarithmic scale. A systematic increase of the width of the bands with $v'$ is observed similar to the case of Xe /3/. A comparison of the observed red shift in absorption relative to the gas phase (table 1) with the emission data of Tinti and Robinson /1/ leads to the Stokes'shift between absorption and emission listed also in table 1.

Emission spectra have been taken for the excitation of each vibrational level $1\leq v'\leq 6$ of the A state. The emission spectra show progressions of Vegard Kaplan bands A ($v'$) $\rightarrow$ X ($v''$). Besides emission from the initially excited vibrational level also emission from lower vibrational levels of the A state is observed in generally. The steady state populations are derived from the intensities of the progressions as described in ref. 3. Each vertical histogram in Fig. 3 corresponds to an emission spectrum and the bars give the steady state populations of the vibrational levels in the relaxation cascade for a nominal concentration of 8%. The population distribu-


Table 3 - Gas to matrix red shift $E_{gm}$, Stokes'shift $E_s$ and radiative lifetime $\tau$ of the A $^3\Sigma_u^+$ transition.

<table>
<thead>
<tr>
<th></th>
<th>$E_{gm}$ (meV)</th>
<th>$E_s$ (meV)</th>
<th>$\tau$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>21 $\pm$ 2</td>
<td>5 $\pm$ 2</td>
<td>0.4 /1/</td>
</tr>
<tr>
<td>Kr</td>
<td>22 $\pm$ 5</td>
<td>10 $\pm$ 5</td>
<td>0.014 /1/</td>
</tr>
<tr>
<td>Xe</td>
<td>40 $\pm$ 4 /3/</td>
<td>7 $\pm$ 1 /3/</td>
<td>0.0015 /2, 3/</td>
</tr>
</tbody>
</table>

For a nominal concentration of 2% N$_2$ in Kr (not shown) contain for excitation of 1$\leq v'\leq 5$ only a population of the initially excited vibrational levels and show no relaxation at all to lower vibrational levels. 80% of the population remain in $v'=6$, 20% relax to $v'=4$ and all other vibrational levels remain empty when the $v'=6$ level is excited.

Fig. 3 - Population distributions (see Fig. 1) for nominal 8% N$_2$ in Kr and Ar crystals at 20 K.

IV - DISCUSSION

N$_2$ in Kr
The low concentration data of nominal 2% N$_2$ in Kr show especially for 1$\leq v'\leq 5$ that there is no vibrational relaxation in the A state of well isolated single N$_2$ molecules in a Kr matrix.

The higher concentration data of nominal 8% N$_2$ in Kr (Fig. 3) demonstrate that vibrational relaxation is initiated by an increasing amount of closely spaced N$_2$ molecules and that the interaction of N$_2$ molecules causes vibrational relaxation.

The vibrational relaxation takes place exclusively in steps of $\Delta v'=2$ up to $v'=3$. These observations can only be explained by a conversion of two A vibrational quanta to one quant of the ground state X. The small excess energy of about 30-50 meV has to be dissipated to matrix phonons. The number of emitted phonons which have an energy of about 5 meV amounts to $\approx 10$ for the $\Delta v'=2$ step process compared to a number of about 35 for the direct nonradiative relaxation between two successive vibrational levels in the A state. The generally expected exponential decrease of the nonradiative rate constants with the number of emitted phonons makes a higher rate constant for the more complicated $\Delta v'=2$ process plausible compared to the direct $\Delta v'=1$ process.

The first step in the relaxation cascade is a $\Delta v'=2$ process also for 4$\leq v'\leq 6$ but in the lower part of the cascades also the intermediate levels are populated (Fig. 3). For $v'=4$ two successive $\Delta v'=2$ processes are expected which consequently lead to an accumulation of two ground state vibrational quanta. The excess energy for the con-
version of two ground state quanta into three vibrational quanta of the A state is also only about 40 meV. Therefore this $\Delta v'=3$ up conversion has a similar rate constant as the $\Delta v'=2$ relaxation. In this up conversion process vibrational energy from the electronic ground state is transferred back into the excited electronic state A causing an increase of the total energy stored in this molecule. The $\Delta v'=3$ process feeds the intermediate levels in the cascades for $4\Delta v'>6$.

The qualitative observations for $N_2$ in Kr are very similar to those for $N_2$ in Xe /3/ which is evident from a comparison of Figs. 1 and 3. Therefore also the quantitative model developed for $N_2$ in Xe /3/ has been applied for $N_2$ in Kr. The rate constants for the $\Delta v'=2$ processes follow from a nonradiative nonresonant electronic energy transfer between two $N_2$ molecules involving the decay of the primarily excited molecule from $A (v') + X (v''=1)$ and the excitation of the neighbouring molecule from $X (v''=0) + A (v'-2)$. The $\Delta v'=3$ process is composed of a decay $A (v') + X (v''=0)$ and an excitation $X (v''=2) + A (v'+3)$.

The rate constants are determined from the molecular Franck-Condon factors, the overlap integrals of the corresponding absorption and emission spectra for the coupling to the phonons and the distance dependent exchange interaction of $N_2$ molecules for the electronic matrix element /3/. The population distributions finally reflect the balance between radiative decay and nonradiative relaxation for the different $N_2$-$N_2$ separations in the matrix. The experimental population distributions in Fig. 3 can be described by this model with contributions from nearest neighbour $N_2$-$N_2$ pairs of 50%, next nearest neighbour $N_2$-$Kr$-$N_2$ configurations of 25% and isolated molecules of 25%.

The influence of the matrix concerns the radiative lifetime and the overlap integrals. The radiative lifetime increases by a factor of 10 in going from a Xe to a Kr matrix (table 1). The overlap integrals go down and the resulting rate constants for vibrational relaxation decrease by factors between 10 and 200. Both effects compensate each other to a large extent in the population distributions which are sensitive to the competition of relaxation and radiative decay. Therefore the qualitative features in the population distributions in Xe and Kr matrices are very similar. Mainly the faster decrease in the phonon wings of the absorption bands in the Kr matrix (Fig. 2) compared to the Xe matrix reduces the overlap integrals whereas changes in the energy mismatches by the Stokes'shifts are of minor importance.

$N_2$ in Ar

Excitation of $A (v'=1)$ in an Ar matrix leads to an efficient relaxation to $v'=0$ (Fig. 3). This immediately evident efficient $\Delta v'=1$ relaxation is the most important observation in the Ar matrix and it has no counterpart in Kr and Xe matrices. In going to higher vibrational quanta in an Ar matrix it is clear that the relaxation cascade is a superposition of $\Delta v'=2$ and $\Delta v'=1$ processes. The $\Delta v'=2$ processes are rather prominent in the first relaxation steps for excitation of $v'=3, 4, 5, 6$. The $\Delta v'=1$ steps are clearly seen for excitation of $v'=1, 2, 3$.

One way to disentangle this rather complex interplay of $\Delta v'=1$ and $\Delta v'=2$ steps would be to go to very low concentrations. In this case the $\Delta v'=2$ processes which require the interaction of two $N_2$ molecules would die out and only the $\Delta v'=1$ processes due to direct dissipation of one vibrational quant into matrix phonons in an isolated $N_2$ molecule would remain. The nice spectra, decay and swell curves of Creuzburg /2/ which have been taken at much lower concentrations presumably represent this case. In our experiments the absorption coefficients would become too small. In analysing our data we have applied the previous described model for the $\Delta v'=2$ processes with the lineshape of the absorption bands in an Ar matrix (Fig. 2) and the energy mismatches given by the Stokes'shifts in Ar (table 1). The rate constant for the $\Delta v'=1$ processes has been assumed to be independent on $v'$. The value of $3 \text{s}^{-1}$ follows from the ratio of relaxed and unrelaxed emission for excitation of $v'=1$ together with the radiative lifetime. Concerning the $\Delta v'=2$ processes this analysis yields rate constants which are in general a factor of 5 smaller than in Xe but significantly larger than in Kr. The reason is the lineshape of the absorption band which lies between Kr and Xe (Fig. 2). The radiative lifetime is even longer than in Kr. Therefore the population in $N_2$ nearest neighbour pairs relaxes very fast by $\Delta v'=2$ processes compared to radiative decay of $\Delta v'=1$ steps. Radiative decay and $\Delta v'=1$ pro-
cesses are both very slow (2.5 s\(^{-1}\) and 3 s\(^{-1}\)) but of similar magnitude. Therefore the bottle necks for \(\Delta v'=2\) steps at \(v'=1\) which appear especially for excitation of \(v'=1, 3, 5\) are finally bridged by \(\Delta v'=1\) processes.

The rate constant for the \(\Delta v'=1\) steps seems to be matrix dependent. A value of 3 s\(^{-1}\) would have been detectable in the Kr matrix. The absence of \(\Delta v'=1\) steps in Kr is an indication that the rate constant is larger in Ar than in Kr. The mean phonon energies of the Ar matrix are about 1-2 meV i.e. about 20% larger than those of a Kr matrix. The number of phonons involved in the \(\Delta v'=1\) radiationless relaxation can be smaller in the Ar matrix and the rate constant larger.

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