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TEMPERATURE DEPENDENCE OF THE EXCITON PHONON COUPLING IN THE STRONG COUPLING LIMIT: RESULTS FOR SOLID NITROGEN

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Temperature dependence of the exciton phonon coupling in the strong coupling limit: results for solid nitrogen*

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Abstract

High resolution (ΔE = 0.75 meV) absorption profiles of the vibronic bands in the range of the $w\,^1\Delta_u \leftarrow X\,^1\Sigma_g^+$ and $a\,^1\Pi_g \leftarrow X\,^1\Sigma_g^+$ exciton progressions at $h\nu \approx 8{,}9$ eV in solid N_2 have been measured in the temperature range between 6 K and 30 K. These excitations are strongly localized so that the observed temperature dependence of the fine structure, consisting of a zero phonon line and a phonon side band, can be described very well in the model of strong exciton phonon coupling at point defects. The experimental results for the $w\,^1\Delta_u$ transition are found to be consistent with the assumption of a Debye spectrum for the phonon density of states and we derive a value for the Debye temperature of Θ = 78 K, which is in very good agreement with that derived from other measurements.

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1. Introduction

The width and shape of molecular absorption bands in the solid phase and their temperature dependence provide important information on relaxation processes and intermolecular interactions. As a prototype simple molecular crystal, solid nitrogen has been the subject of many studies involving absorption- and reflection- [1-8], energy loss- [9], matrix isolation- [6,8,10-12] and photoelectron-spectroscopy [13,14] for the investigation of its electronic structure. Despite this extensive work, until recently there has been no detailed analysis of the absorption line shape of the exciton bands which is of fundamental importance for an understanding of the exciton-phonon coupling in vibrating molecular crystals and for a critical evaluation of the available calculations and theoretical predictions e.g. [15-20].

In solid N_2 where the molecules are held toghether by the weak van der Waals forces the electronic excitation of the molecules can be described by Frenkel excitons, which interact with the crystal only via resonance interaction. For the two transitions $a\,^1\Pi_g \leftarrow X\,^1\Sigma_g^+$ and $w\,^1\Delta_u \leftarrow X\,^1\Sigma_g^+$ with small oscillator-strength the interaction is very weak and therefore the excitations are strongly localized. The main interaction of the excited state with the crystal is then an exciton phonon coupling [15].

Recent quantitative high-resolution absorption measurements for solid N_2 in the range of the $w\,^1\Delta_u \leftarrow X\,^1\Sigma_g^+$ and $a\,^1\Pi_g \leftarrow X\,^1\Sigma_g^+$ derived exciton progressions revealed a detailed fine structure of the vibrational bands [7,8]. In Fig. 1 the fine structure of a band of each transition is shown.

On the low energy wing of each band one can clearly see the sharp zero phonon line (ZPL) ($\hbar\omega$=meV), and to higher energies the phonon side band , which consist of the one-two and multi-phonon excitations of the N_2-lattice . For the analysis,model calculations had been performed[7] for zero K temperature which were based on a local picture treating the lattice dynamics in a "supermolecule model"[20], in which only a few shells around the excited molecule are allowed to participate in the nuclear motions.

In the present experiment we have investigated the temperature dependence of the line shape for both above mentioned transitions. Further, we have determined the oscillator strength as a function of temperature for a particular vibrational band for both transitions. Instead of using the "supermolecule model" for the analysis we compare our experimental results with the theoretical predictions based on exciton phonon coupling in the strong coupling limit originally developed for point defects(e.g.[21,22]).

In the harmonic approximation and with linear coupling, the intensity of the n-th phonon excitation is determined by a poisson distribution[21]

$$I_n/I_{ges} = e^{-S} \cdot S^n/n! \qquad (1)$$

S is the coupling parameter, which describes the strength of the phonon coupling to the electronic excitation. For the transition $a^1\Pi_g \leftarrow X^1\Sigma_g^+$ the parameter S is larger and therefore the phonon side band for this excitation is more intense (see Fig. 1).

With a known phonon occupation number $n(\omega)$ and a coupling function $D(\omega)$ the coupling parameter S can be calculated[22]:

$$S(T) = \int_{-\infty}^{\infty} d\omega D(\omega) \cdot (2n(\omega)+1) \qquad (2)$$

Because of the temperature dependence of the occupation number for the phonon states, the coupling parameter S becomes temperature dependent and the spectrum changes with temperature.

2. Experimental details

The experiments have been performed with synchrotron radiation from the storage ring DORIS at DESY. An extensive description of the experimental details may be found in Ref. 8. Quantitative high resolution ($\Delta\lambda$ = 0.15 Å) absorption spectra were recorded using the 3m normal incidence monochromator HONORMI[23]. Light from the exit slit of the monochromator traversed a film of solid N_2 condensed on a LiF window. The transmitted light was detected by a solar blind photomultiplier (EMR 542F-08-18). The samples have been prepared by freezing N_2 gas under ultrahigh vacuum conditions ($p = 5 \times 10^{-10}$ Torr) onto the cooled substrate. The temperature was varied between 6 and 30 K and the temperature was measured with an accuracy of 1 K by a carbon resist thermo-element. The sample gas was nitrogen of A52 grade from Air Liquide. Its purity was checked during condensation by a mass spectrometer. With this improved sample preparation technique we were able to prepare samples which showed very sharp spectral features (see Fig. 1) limited mainly by the monochromator resolution.

An experimental problem arises at low temperatures, when the ZPL is very sharp and therefore its measured half-width and intensity is strongly influenced by the resolution of the monochromator[24]. To partly solve this problem we have developed a computer programm in which the measured half-width and area below the ZPL are transformed into the real values using a Gaussian of known width as the resolution function of the monochromator[8]. Note that this correction of the measured spectra is only relevant for sharp spectral features at low temperatures and is the main reason for the error bars in Fig. 3 for the data points below ≈18 K.

3. Results and discussion

In Fig. 2 the fine structure of the v'=0 band of the $w^1\Delta_u$ progression is shown, measured at six different temperatures. With increasing temperature, the structure becomes more diffuse and the ZPL loses intensity. At 30 K the ZPL is only a small shoulder in the spectrum. Since the coupling of the excitation to the lattice phonons is temperature dependent (see equation 2) , the fine structure in the spectrum changes when the temperature is varied.

According to equation 1, the coupling parameter S can be derived from intensity measurements of the whole band and of the ZPL:

$$S = \ln(I_{ges}/I_o) \qquad (3)$$

In order to determine the intensity of the ZPL and of the whole band, the measured curve was approximated by a sum of Gaussian curves and the area was derived by integrating these. The experimental results appear in Fig. 3

plotted versus T^2. There the estimated error bars at low temperatures are mainly due to the finite monochromator resolution whereas at higher temperatures they reflect the ambiguity in separating the ZPL from the rest of the band. The experimental values for the ZPL width, the coupling parameter S and the oscillator strength are collected in Table 1.

In order to compare our experimental results with the predictions of the strong coupling model, equation 2 was transformed by assuming a Debye spectrum for the phonon density of states and a Bose-Einstein distribution for the thermal occupation[22,25]. One obtains:

$$S(T) = S(0)\ (1+2\Gamma/3\left(\frac{T}{\Theta}\right)^2) \qquad (4)$$

where Θ is the Debye temperature of the crystal. If one plots the values of S at different temperatures versus T squared, one should obtain a straight line, the slope of which is a function of Θ. Such a plot is shown in Fig. 3 using the values of table 1. The measured values of S are very close to a straight line which is derived by assuming a Debye temperature of Θ = 78 K. This value is in good agreement with that derived from measurements of the specific heat for solid N_2[26]. This is a strong evidence, that the fine structure of the excitation $w^1\Delta_u \leftarrow X^1\Sigma_g^+$ in solid N_2 can be described within the model of strong exciton phonon coupling at point defects, and that obviously all acustical phonons of the N_2 crystal are coupling to the excitation.

The $a^1\Pi_g$ state shows a different behaviour. The evaluation leads to a Debye temperature of 110 K[8], which shows that the coupling to the phonons is not the same as for the $w^1\Delta_u$ state. The reason for this difference is that the transition to $a^1\Pi_g$ remains parity forbidden in the crystal, but the intensity can be enhanced by coupling phonons of odd parity to the excitation. Therefore the oscillator strength of this transition should be temperature dependent.

In Fig. 4 the oscillator strength of one band of the two transitions $a^1\Pi_g \leftarrow X^1\Sigma_g^+$ and $w^1\Delta_u \leftarrow X^1\Sigma_g^+$ is plotted versus temperature. Whereas the $w^1\Delta_u$ excitation is completely temperature independent, the intensity of the $a^1\Pi_g$ band increases drastically with temperature, a behaviour which is typical for a parity forbidden transition[21].

4. Conclusion

The analysis of the temperature dependent line shape for the weak $a^1\Pi_g \leftarrow X^1\Sigma_g^+$ and $w^1\Delta_u \leftarrow X^1\Sigma_g^+$ exciton transitions in pure solid nitrogen has shown that these excitations are strongly localized and can be well described within the model of strong exciton phonon coupling at point defects. The excited molecules in the crystal represent point defects which, contrary to regular permanent point defects, disturb the crystal lattice only slightly and therefore couple to all the phonon branches of the lattice.

Acknowledgement

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Table 1

Experimental values for the temperature dependent zero phonon line width Γ_{ZPL} (in meV), the coupling parameter S, and the oscillator strength for the v' = 0 band of the $w^1\Delta_u \leftarrow X^1\Sigma_g^+$ transition in solid nitrogen.

T (K)	Γ_{ZPL}(meV)	S	f x 10^7
6	0.42	2.12	3.20
15	0.63	2.41	3.18
20	0.94	2.72	3.19
23	1.09	3.10	3.18
25	1.51	3.31	3.19
27	2.05	3.56	3.18
30	2.49	3.91	3.15

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Figure Captions

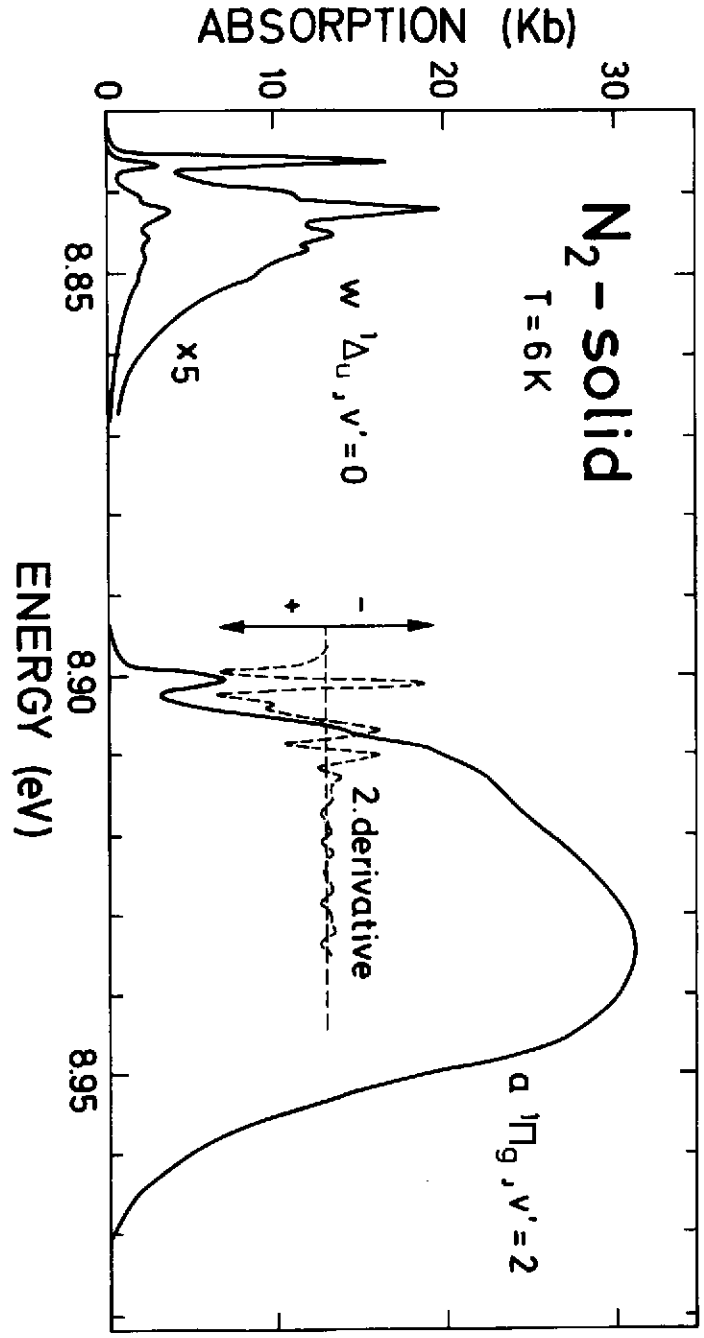
Fig. 1: Absorption spectrum of pure solid N_2 around $h\nu$ = 8.90 eV showing one vibrational band for each of the two transitions $a^1\Pi_g \leftarrow X^1\Sigma_g^+$ and $w^1\Delta_u \leftarrow X^1\Sigma_g^+$.

Fig. 2: Measured temperature dependence of the line shape for the $v' = 0$ band of the $w^1\Delta_u \leftarrow X^1\Sigma_g^+$ transition in solid N_2.

Fig. 3: The coupling parameter S as a function of T^2 for the $v' = 0$ band of the $^1\Delta_u$ - system. The straight line is derived by assuming a Debye - temperature of Θ= 78 K.

Fig. 4: Oscillator strength of the $v' = 0$ band of the $w^1\Delta_u$ and the $v' = 2$ band of the $a^1\Pi_g$ transition as a function of temperature in solid N_2.

Fig. 1


ABSORPTION (Kb)
0
10
20
30
8.85
8.90
8.95
ENERGY (eV)
N2 - solid
T = 6 K
w 1Δu , v' = 0
x5
+
-
2. derivative
a 1Πg , v' = 2

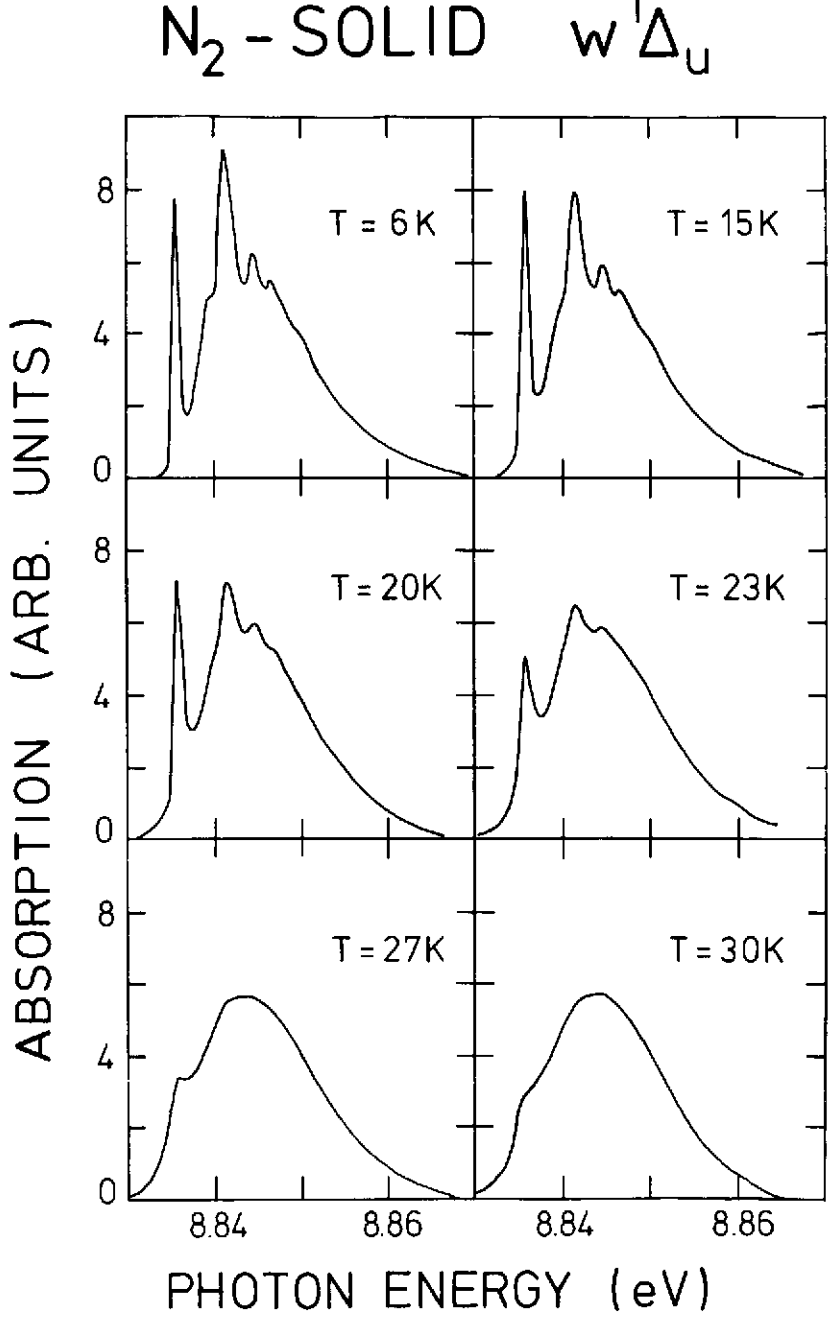
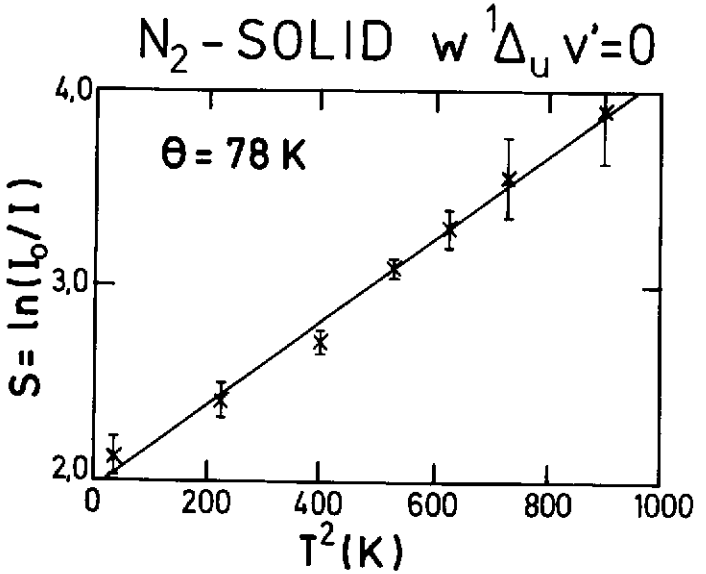

N2 - SOLID w 1Δu
ABSORPTION (ARB. UNITS)
T = 6K
T = 15K
T = 20K
T = 23K
T = 27K
T = 30K
0
4
8
8.84
8.86
PHOTON ENERGY (eV)

Fig. 2


N2 - SOLID w 1Δu v'=0
θ = 78 K
S = ln(I0/I)
T2(K)
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3,0
2,0
0
200
400
600
800
1000

Fig. 3

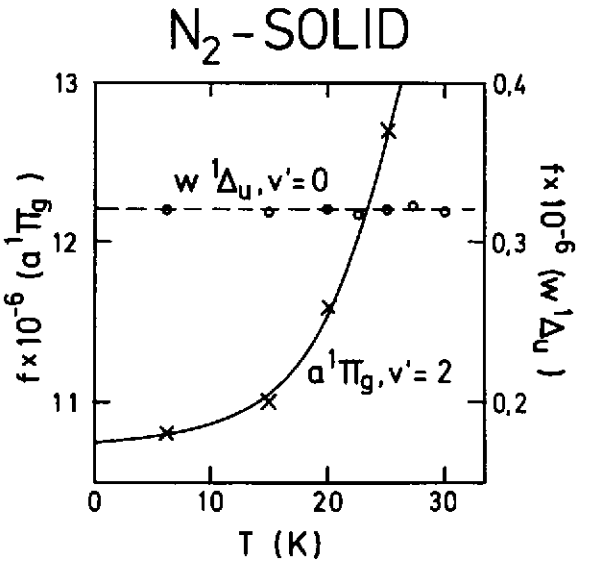
N2 - SOLID
w 1Δu, v'= 0
a 1Πg, v'= 2
f x10-6 (a 1Πg)
f x10-6 (w 1Δu)
T (K)
13
12
11
0,4
0,3
0,2
0
10
20
30

Fig. 4