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Abstract

Results of quantitative high resolution absorption measurements in the range of the $w^1\Delta_u$ and $a^1\Pi_g \leftarrow X^1\Sigma_g^+$ derived exciton progressions in solid N_2 are reported. The newly observed detailed fine structure of the vibrational bands is analysed in terms of a sharp zero phonon line and phonon assisted exciton transitions. A theoretical analysis based on a strong exciton phonon coupling model leads to good agreement with the observed experimental line shape.

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The electronic structure of simple molecular crystals such as solid nitrogen and carbon monoxide has attracted much interest because of their key role for a better understanding of exciton states in weakly bound van der Waals solids. The absorption spectra of solid CO and N_2 provided the first examples for the perturbation of the excited electronic states of simple molecules by the crystal field[1,2]. However, almost no quantitative information has been obtained experimentally on other important features of the absorption. In particular the line shape of the bands has never been analysed, although a detailed understanding of the coupling of exciton states to the crystal might be expected and a number of calculations and predictions for the exciton-phonon coupling in vibrating molecular crystals are available in the literature[3-8].

Recently, high resolution low temperature Vacuumultraviolet Spectroscopy[9-11] has provided new ways for examing higher excited states of van der Waals solids, such as surface excitons in rare gas solids[11] and vibrational and librational excitations of matrix isolated molecules[9]. In the present work we apply these techniques to the investigation of exciton transitions in pure solid nitrogen. A careful examination and analysis of the exciton absorption line shapes for two weak transitions forming extended progressions in the spectral range from 8.5 eV to 12.5 eV will be presented. One of the important results of our study was the detection of extremely sharp (FWHM $\leq$ 1 meV) zero phonon lines (ZPL) and accompanying phonon side bands for each vibrational subband of an electronic excitation.

The experiments have been performed with two different monochromators. By using the 10 m spectrograph located at Meudon (France)[9] we have recorded the spectra at a high resolution of 0.014 Å in first order. The spectrograph was illuminated with a BRV continuum source and calibrated with atomic emission lines. Data obtained with this instrument have been mainly used for establishing accurate energy positions of the bands. Quantitative intensity measurements have been performed at a resolution of 0.15 Å with the 3 m normal incidence monochromator with synchrotron radiation from the DORIS storage ring at DESY (Germany)[10]. This instrument was calibrated by rare gas absorption lines. Light from the exit slit traversed a film of solid N_2 condensed on a LiF window, the temperature of which ranged from 6 K to 35 K. These experiments were carried out under ultrahigh vacuum conditions ($p \simeq 5 \times 10^{-10}$ Torr). The transmitted light was detected by a sodium salycilate photomultiplier (EMI 9804) combination. The sample gas was nitrogen of A 52 grade from Air Liquide. Its purity was checked during condensation by a mass spectrometer. More details will be given in a forthcoming paper[12].

A general view of the absorption of solid N_2 in the range of the $a^1\Pi_g \leftarrow X^1\Sigma_g^+$ and $w^1\Delta_u \leftarrow X^1\Sigma_g^+$ transitions is shown in Fig. 1. Whereas the a-system forms a progression of fairly broad bands the stronger w-system forms a progression of comparatively sharp bands. Both transitions are electrically dipole forbidden in the gaseous phase[13]. They become partly allowed in the lower symmetry of the excited molecular state in the crystal. The symmetry of the free N_2 molecule ($D_{\infty h}$) is reduced to the site symmetry group (C_{3i}) in the α-phase of solid N_2. (This is the low temperature cubic phase for $T \leq 35.6$ K[14].) Thus one would expect a $E_g \leftarrow A_g$ and a $E_u \leftarrow A_g$ transition corresponding to the a- and w-system respectively. Consideration of the factor group T_h of the molecular crystal yields a splitting of the $a^1\Pi_g$ final state into one E_g and two F_g components and of the $w^1\Delta_u$ state into one E_u and two F_u components. Consequently the $g \leftarrow g$ transitions remain electrically forbidden in the crystal, whereas transitions to F_u final states become allowed. We note however already at this point, that our results do not show a factor group splitting. As can be seen from Fig. 1 and Table 1 both progressions have an extremely small oscillator strength even in the crystal.

Comparison of the constants derived from a polynomial fit to the progressions with those known for the corresponding transitions in the gaseous phase shows that both are very similar. Thus e.g. the quanta of the intramolecular vibration for the a-system are 208 meV[13] and 205 meV in the gaseous and solid phase respectively. Solidification leads to an almost rigid shift of roughly 50 meV of all bands towards lower energies.

Compared to previous results[2] our data show a far more detailed fine structure of the various bands. As an example we show in Fig. 2 the range of the v' = 0 band of the $w^1\Delta_u$ system and the v' = 2 band of the $a^1\Pi_g$ system. Although both bands are quite different in their general appearance we note that they show as a common feature a very sharp line at the low energy side followed by broader partly structured features towards higher energies. As shown by the second derivative of the v' = 2 band these features are very similar for both systems as far as the spacings are concerned (see also Table 1).

The splitting of the bands of the a-system has been discussed as a Davydov splitting by Brith and Schnepp[2]. We reject this interpretation since the observed detailed structure with its constant splitting over the progression is not compatible with a simple Davydov splitting into two components. Instead of such an explanation, which is applicable in a weak exciton phonon coupling case, we propose an analysis for the fine structure based on a polaron model[5] with strong exciton phonon coupling[3,5,6,7,15].

Within this model we interprete the sharp maximum appearing on the low energy side of each vibrational band as the zero phonon line (ZPL). The electronic excitation leads to a strong localized deformation of the crystal. The features at higher energies correspond to the coupling of the electronic excitation to lattice modes in the deformed potential at this site. For the v' = 0 band of the w-system we can readily identify several phonon sidebands corresponding to the excitation of one or more phonons. Their energies are listed in Table 1 together with data for the higher vibrational bands of this as well as for the $a\Pi_g$-progression.

To further substantiate this analysis we have performed calculations for 0 K temperature which are based on the following assumptions[16,17]: (i) the exciton-phonon coupling is linear in its external coordinates; (ii) the external oscillators are harmonic and (iii) only one translational ω_T and one librational ω_L mode are coupled to the exciton state. In order to simulate the experimental curve, the one-phonon shape was chosen to be doubly peaked at ω_T = 5.9 meV and ω_L =3.7 meV. These frequencies are close to the known values of the librational and the translational modes of the vibrating N_2 crystal as observed by Raman and infrared-spectroscopy[18,19]. The higher phonon sideband was obtained by convoluting the one-phonon band k-times with itself and weighting with a Poisson distribution of the following form[15-17]: $P_k = S^k e^{-S}/k!$, where S is the coupling strength[15], and e^{-S} represents the ratio of the ZPL intensity to the integrated intensity of the entire band. The result of this calculation with a value of S = 2.2 is shown for the v' = 0 band of the w-system in Fig. 3. The agreement with the experimental results is very good, thus verifying our analysis of the shoulder at around 4.0 meV above the ZPL as a librational mode of the excited N_2-molecules and the mode with $\omega_T \approx 5.7$ meV as the translational mode of the vibrating N_2 crystal. Although apparently the same modes are excited in the w- and in the a-system (see Table 1) the coupling strength for the a-system is much greater leading to an enhancement of the multiphonon processes.

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Table 1: Excitation energies (in eV) for the zero phonon lines (ZPL) in solid N_2 for the $a^1\Pi_g$ and the $w^1\Delta_u$ progressions for v' < 6 and energetic positions of the phonon induced fine structure with respect to the ZPL (in meV). For each vibrational band the oscillator strength f is given. Positions of the ZPL for the a-system given in brackets have been estimated

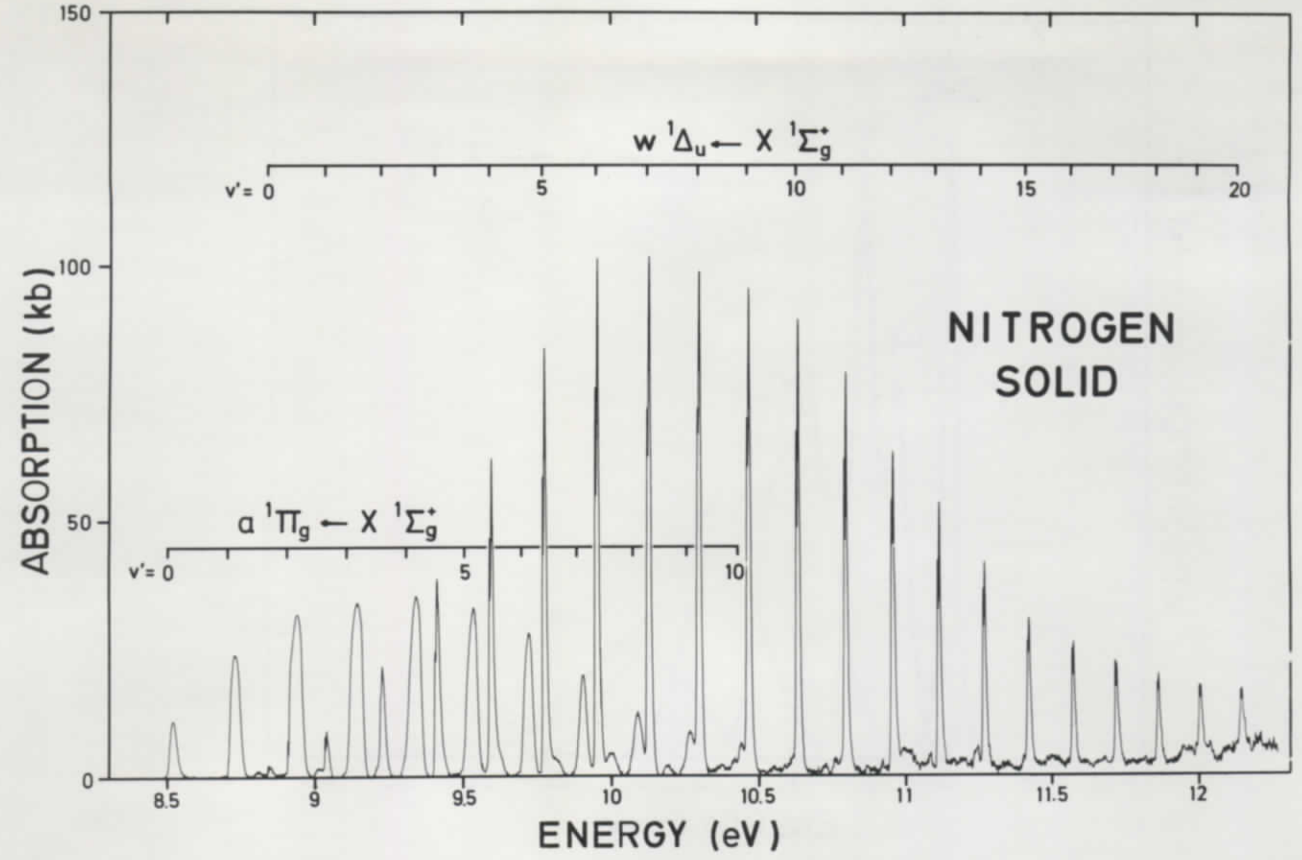
	$a\Pi_g \leftarrow X^1\Sigma_g^+$						$w^1\Delta_u \leftarrow X^1\Sigma_g^+$						
v'	ZPL (eV)	Δ1 (meV)	Δ2 (meV)	Δ3 (meV)	Δ4 (meV)	f (x 10^{-6})	ZPL (eV)	Δ1 (meV)	Δ2 (meV)	Δ3 (meV)	Δ4 (meV)	Δ5 (meV)	f (x 10^{-6})
0	8,496	-	4,5	8,6	12,0	2,7	8,835	4,0	5,7	9,0	10,9	14,8	0,3
1	8,701	-	4,5	8,6	12,4	8,1	9,026	3,4	5,7	8,6	11,0	-	1,4
2	8,903	2,6	5,8	8,7	11,6 -	11,8	9,214	-	5,6	-	11,6	-	3,7
3	9,106	-	5,4	10,2	-	13,8	9,398	-	6,6	-	12,0	-	6,8
4	(9,305)	-	-	-	-	13,4	9,580	-	5,8	-	12,0	-	9,4
5	(9,502)	-	-	-	-	10,4	9,760	-	5,8	9,0	11,4	-	10,3

Figure captions

Fig. 1 Overview of the absorption spectrum from solid Nitrogen in the photon energy range from 8.5 eV to 12.3 eV. The two progressions corresponding to the gas phase $a^1\Pi_g \leftarrow X^1\Sigma_g^+$ and $w^1\Delta_u \leftarrow X^1\Sigma_g^+$ transitions are labelled. Note that we have chosen the zero phonon features at the low energy sides of the bands as the origins.

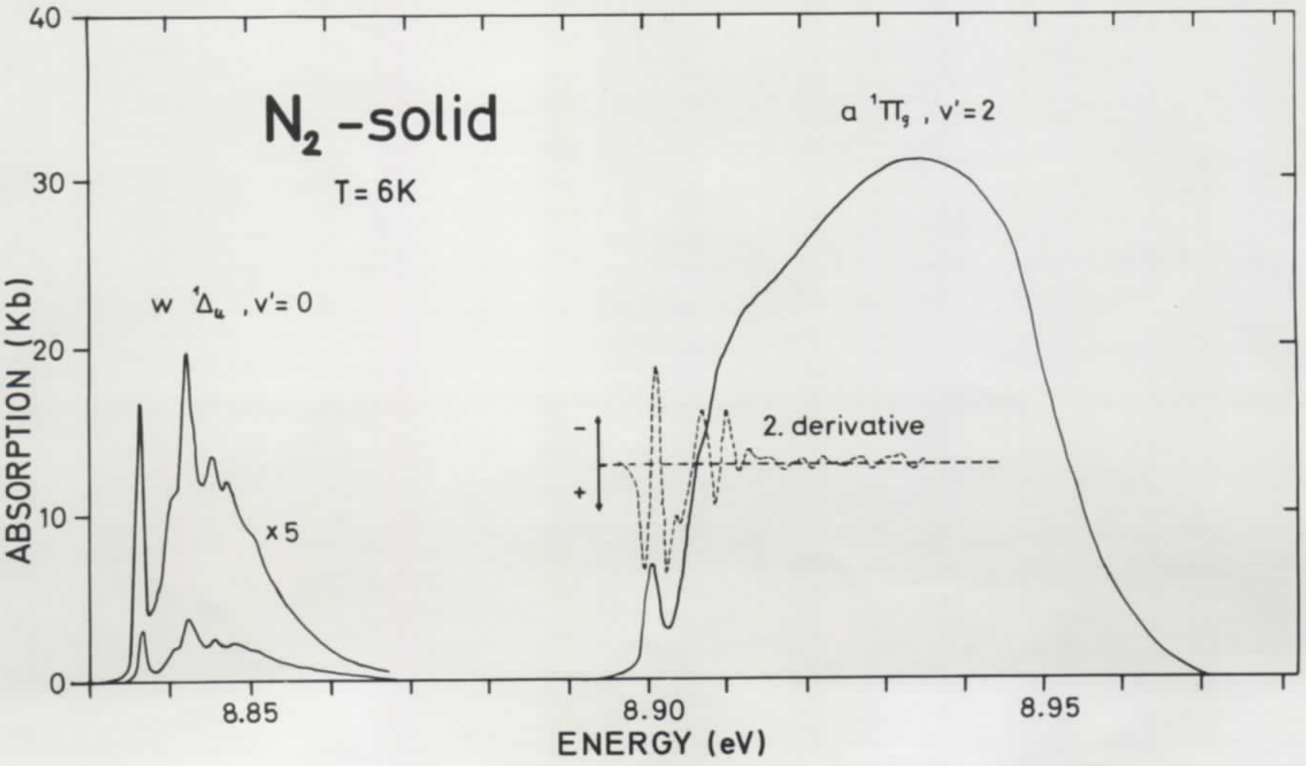
Fig. 2 Absorption spectrum of solid N_2 at 6^0K in the range 8.83 eV to 8.98 eV. For the v' = 2 band of the $a^1\Pi_g$ system the second derivative is also shown.

Fig. 3 Simulated line shape of the v' = 0 band of the $w^1\Delta_u \leftarrow X^1\Sigma_g^+$ system at T = 0 with a coupling strength of S = 2.2. For details see text.



ABSORPTION (kb)
0
50
100
150
ENERGY (eV)
8.5
9
9.5
10
10.5
11
11.5
12
$w\ ^1\Delta_u \leftarrow X\ ^1\Sigma_g^+$
v' = 0
5
10
15
20
$a\ ^1\Pi_g \leftarrow X\ ^1\Sigma_g^+$
v' = 0
5
10
NITROGEN
SOLID

Fig. 1



ABSORPTION (Kb)
0
10
20
30
40
ENERGY (eV)
8.85
8.90
8.95
N_2 -solid
T = 6K
$w\ ^1\Delta_u$, v' = 0
x 5
$a\ ^1\Pi_g$, v' = 2
2. derivative
-
+

Fig. 2

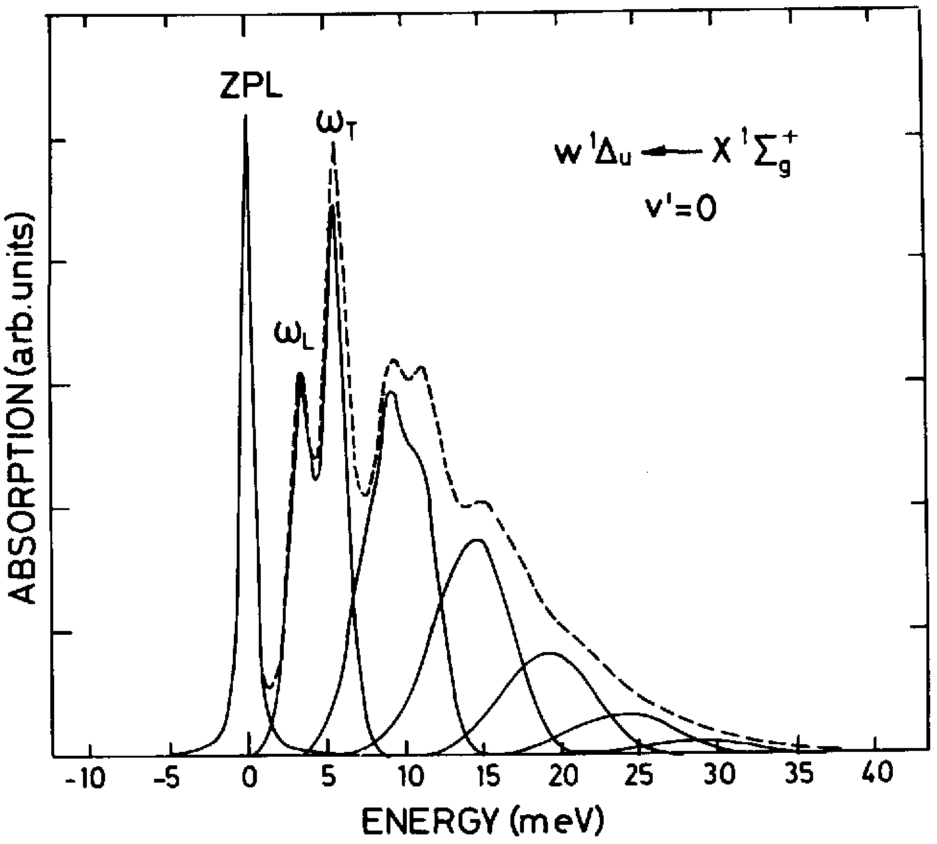

ZPL
ω_T
ω_L
$w\,^1\Delta_u \longleftarrow X\,^1\Sigma_g^+$
$v'=0$
ABSORPTION (arb.units)
-10
-5
0
5
10
15
20
25
30
35
40
ENERGY (meV)

Fig. 3