K. Yvon for many interesting discussions. Finally we thank M. Wenger for preparing the computer program for the modified equation for H_{c2}.

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Experimental Deperturbation of the $b\,{}^1\Pi_u \leftarrow X\,{}^1\Sigma_g^+$ Transition of N_2 in the Solid State, Pure and Trapped in Ne and CF_4 Matrices at Low Temperature*

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The progression observed below 1000 Å in spectra of solid N_2, pure and trapped in Ne and CF_4 matrices at 4.2 K, is ascribed to the valence transition $b\,{}^1\Pi_u \leftarrow X\,{}^1\Sigma_g^+$ of N_2. As previously observed in the similar case of NO, the regularity in intensity distribution and in vibrational spacings indicates the absence of the Rydberg transition $c\,{}^1\Pi_u \leftarrow X\,{}^1\Sigma_g^+$ responsible for strong perturbations in the free-molecule spectrum.

Optical absorption studies of condensed gases are usually limited by the transmission cutoff of the LiF substrate[1] (1050 Å). However, Baldini, using an unconventional technique, extended the investigations on solid rare gases at 20 K down to 900 Å. The hydrogen spectrum which he used as a source was too weak below this wavelength.[2] In order to overcome this limitation we have built a new apparatus for absorption studies at 1.5 K and down to 500 Å, with a triggered vacuum spark as a source of continuum.[3,4]

As an extension of the study of homogeneous interactions of Rydberg states with valence states, as previously observed for NO trapped in rare-gas matrices by Roncin, Damany, and Romand,[1] we have investigated the absorption spectrum of N_2 below 1050 Å in both the pure solid and in Ne and CF_4 matrices. In this region of the free-molecule spectrum, the valence states $b\,{}^1\Pi_u$ and $b'\,{}^1\Sigma_u^+$ interact strongly with the nearby Rydberg states $c\,{}^1\Pi_u$ and $c'\,{}^1\Sigma_u^+$. These interactions give rise to strong irregularities in intensity and also in vibrational spacing corresponding to the crossing of energy-potential curves of valence states and Rydberg states of the same symmetry.[5,6] Although the free-molecule spectrum has long been known,[7-9] only recently has a consistent classification of the bands been proposed.[5,6,10]

Records of solid-N_2 absorption spectra are shown in Fig. 1 (below 900 Å no clear structure has been detected). They correspond to an estimated thickness of less than 1000 Å in matrices, the dilution being about 1%. Unlike the sharp bands observed[1,3] above 1000 Å (full width at half-maximum about 100 cm^{-1} in the pure solid and about 80 cm^{-1} in a Ne matrix for the $w\,{}^1\Delta_u \leftarrow X\,{}^1\Sigma_g^+$ transition), the bands reported here are somewhat diffuse in the pure solid and slightly sharpened on isolating N_2 in Ne or CF_4 matrices (full width at half-maximum ≅300 cm^{-1}).

Incidentally we have obtained for the first time the absorption spectrum of solid CF_4. The onset of absorption of a 1000-Å thick deposit is at about 930 Å (13.3 eV), in agreement with the high value of the first ionization potential (≅15.5 eV).[11-13]

In the free-molecule spectrum the bands arising from the $b'^1\Sigma_u^+ \leftarrow X\,^1\Sigma_g^+$ transitions are much less intense than those coming from the $b\,^1\Pi_u \leftarrow X\,^1\Sigma_g^+$ transition so that their contribution to the width of the bands observed in the solid seems to be negligible. We therefore assigned all of them to the prevailing $b\,^1\Pi_u \leftarrow X\,^1\Sigma_g^+$ transition. Two remarkable features can be observed in the spectra of solid N_2: (i) The intensity distribution is regular within the progression, and (ii) although the bands are somewhat broad, the inaccuracy of ±40 cm^{-1} in their measurement is well below the irregularities arising from perturbations in the gas phase. It can be consequently asserted that in the pure solid as well as in matrices the vibrational spacings become regular and fit the calculated deperturbed values well.[14] From these observations we conclude the Rydberg transition $c \leftarrow X$ is absent. As previously discussed in the similar case of NO trapped in matrices,[15] the disappearance of the Rydberg transition is attributable to the strong interaction of the large Rydberg orbital with the environment. In Table I are summarized our assignments with respect to the gas-phase val-

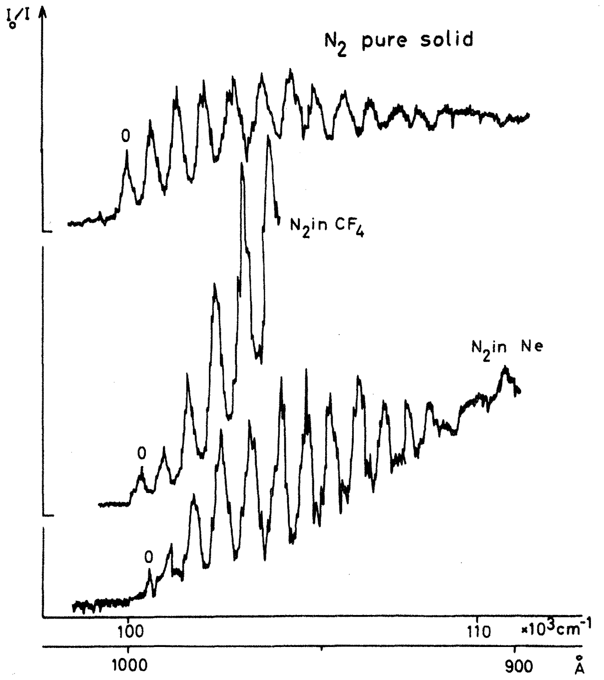

FIG. 1. Absorption spectra of pure solid N_2 and of N_2 trapped in Ne and CF_4 matrices at 4 K.

Table I. Wave number ν and vibrational spacing ΔG of solid N_2 pure and trapped in Ne and CF_4 matrices compared with the gas-phase values and with the deperturbed values. (ν and ΔG in cm^{-1}.)

	N_2 gas [a]		deperturbed [b]		N_2 solid [c]		N_2 in Ne [c]		N_2 in CF_4 [c]	
v'	ν	ΔG	ν	ΔG	ν	ΔG	ν	ΔG	ν	ΔG
0	100816.9		100817		100120		100796		100573	
		634.8		637		565		623		621
1	101451.7		101454		100685		101420		101194	
		700.0		717		735		631		679
2	102151.7		102171		101420		102051		101873	
		711.9		749		715		724		733
3	102863.6		102920		102135		102775		102606	
		685.2		768		788		841		807
4	103548.8		103688		102923		103616		103413	
		1151.4		784		855		790		732
5	104700.2		104472		103778		104406		104145	
		646.2		795		814		802		787
6	105346.4		105267		104592		105208		104932	
		764.2		793		760		768		715
7	106110.6		106064		105352		105976		105647	
		822.7		787		780		805		705
8	106933.3		106851		106132		106781		106352	
		710.2		769		786		700		
9	107643.5		107620		106918		107481			
		728.9		750		763		744		
10	108372.4		108370		107681		108225			
		747.6		736		749		740		
11	109120.0		109106		108430		108965			
		711.1								
12	109831.1									

[a] Ref. 10.

[b] Ref. 14.

[c] This work.

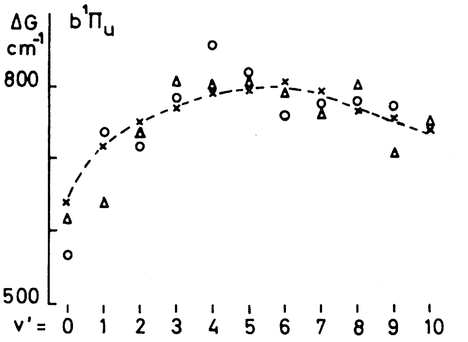

FIG. 2. Comparison between the vibrational spacings $\Delta G(v')$ deduced from our measurements and the calculated deperturbed values. Crosses: deperturbed (Ref. 10). Circles: pure solid N_2 (this work). Triangles: N_2 in Ne (this work).

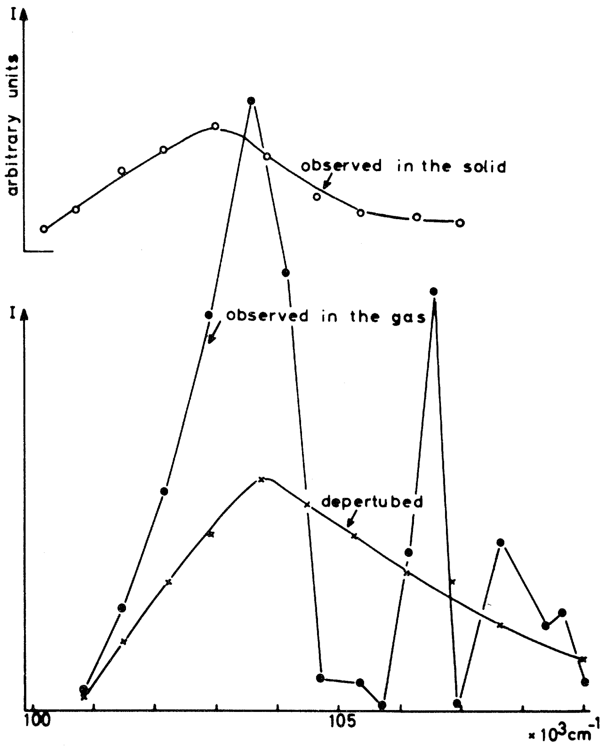

FIG. 3. Intensity distributions illustrating the deperturbation of the electronic state in pure solid N_2 with respect to the free molecule (Ref. 14).

ues[10] along with the deperturbed values.[14] As the site dimension ρ_s of the matrix increases from Ne ($\rho_s = 3.51$ Å[15]) to CF_4 ($\rho_s \cong 4.60$ Å[16]), the absorption spectrum is shifted more to the red. The magnitude and the direction of the shifts are in agreement with previous discussions.[15,17] In Fig. 2 the vibrational spacings ΔG are plotted versus the vibrational quantum number v' using the data of Table I. Figure 3 shows a comparison between the relative intensities in the solid, the gas-phase values,[9] and the calculated deperturbed values.[14]

Our results are not in so good agreement with the recent reflection measurements of Buxton and Duley on pure solid N_2.[18] The intensity distribution of the bands is similar, but in their spectrum they still observe some irregularities in the vibrational spacings. We have detected one more term on the long-wavelength side which we assigned to the transition towards $v' = 0$ of the $b\,{}^1\Pi_u$ state. This would lead to a shift, between our absorption data and their reflection measurements, of 500 cm^{-1} which seems to be large compared with the similar case of CO.[19]

By increasing the thickness of the deposit up to 10 000 Å the bands merge into the absorption background which anomalously decreases towards shorter wavelengths. This anomalous shape could be tentatively ascribed to a luminescence of solid N_2, as recently discussed in a similar case by Morris and Angus.[20] This luminescence light, of much longer wavelength, is detected by the photomultiplier and contributes to lowering the ratio I_0/I in the region below 1000 Å where N_2 absorbs strongly.

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New Analysis of Direct Exciton Transitions: Application to GaP

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A new analysis of direct exciton data is presented and applied to the $E_0, E_0+\Delta_0$ transitions in GaP. A curve-fitting procedure is used to compare both the discrete and continuum structure in the data with theoretical curves. Good agreement is obtained for the binding energies, broadening, strengths, and shapes. It is shown that the binding energy of E_0 is 11 ± 1 meV rather than the 5-6–meV value previously obtained from the conventional analysis.

We have reexamined the absorption data of Dean, Kaminsky, and Zetterstrom[1] for the direct exciton (E_0) and the spin-orbit split-off exciton ($E_0+\Delta_0$) in GaP. In our new analysis the exciton binding energy and the broadening are determined from a comparison of the data with the theoretical spectrum including both the discrete and continuum contributions. We show that the experimental shapes, strengths, and binding energies of these excitons are well accounted for by recent refinements[2] of the simple Wannier exciton theory.[3] A new value of 11 meV is obtained for the E_0 exciton binding energy which is considerably larger than the previous estimates of 5-6 meV.[1,4] We believe that our results convincingly demonstrate that this new, but yet very basic, method of analysis can provide a stringent comparison between theory and experiment.

The 25-K absorption data of Dean, Kaminsky, and Zetterstrom[1] are shown as the solid curve in Fig. 1. This structure results from electronic transitions from the highest valence band to the lowest conduction band near $k=0$. The splitting between E_0 and $E_0+\Delta_0$ is caused by the well-known spin-orbit splitting of the six valence states into a fourfold (E_0) and a twofold ($E_0+\Delta_0$) degenerate state at $k=0$. In addition to these direct transitions, we estimate that indirect transitions ($\Gamma \to X$) contribute a rather flat background absorption of approximately 1000 cm^{-1} in this region.

The $E_0+\Delta_0$ structure is an example of the well-known "textbook" case of a Wannier exciton with a hydrogenic series of discrete levels with energies

$$E_n = E_g - \mu e^4/2\epsilon_s^2\hbar^2 n^2 = E_g - R_0^*/n^2, \tag{1}$$

where E_g is the band gap, μ is the reduced mass [$\mu^{-1} = m_c^{*-1} + m_{\text{s.o.}}^{*-1}$ for the conduction (m_c^*) and split-off ($m_{\text{s.o.}}^*$) bands], ϵ_s is the static dielectric constant, and R_0^* is the effective Rydberg. The total absorption coefficient (for no broadening) consists of the discrete lines (among which the 1s state predominates) plus the exciton

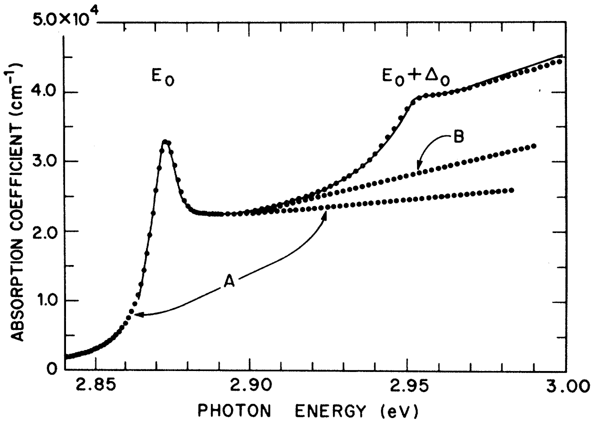

FIG. 1. Direct E_0 and $E_0+\Delta_0$ exciton absorption of GaP at 25 K. The solid curve is the data of Dean, Kaminsky, and Zetterstrom, Ref. 1. The dotted curves are the various theoretical fits discussed in the text.