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The absorption spectrum of H_2 molecules in a Ne-Matrix in the energy range of 11eV to 12,2eV due the vibrational levels $v' = 0,\dots,7$ of the $B^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ Rydberg transition is reported.

1. Introduction

Rydberg states of atoms like Xe, Kr and Ar (1-4) and of small molecules (3) like C_2H_2, C_2H_4, CH_3I, C_6H_6(4), NO(5), $C_{10}H_8$(6), CS_2, COS(7) have been observed in solid rare gas matrices. The stong interaction of Rydberg transitions with the lattice of the matrix manifests itself in large blue shifts and strong broadening. It raises questions concerning the conditions for the persistence of Rydberg states at the nuclear configuration of the ground state which is monitored in absorption experiments (1-8) and concerning the magnitude of lattice rearrangements initiated by these excited states (2,3,5). This strong interaction has been exploited for an experimental deperturbation of valence transitions in NO(5) and N_2(8). Absorption experiments have been performed in pure solid H_2 and D_2(9,10,11) and on H and D atoms in Ar(12) and an H atoms in Ne matrices (13). The absorption spectra available for H_2 and D_2 molecules in rare gas matrices cover the photon energy range from 13-20eV (11) but exclude the range of the lowest Rydberg transition (Lyman bands) $B^1\Sigma_u^+\ 2p\sigma \leftarrow X^1\Sigma_g^+\ 1s\sigma$ which lies in the gas phase between 11 and 13eV. Mulliken has classified this transition as "semi-Rydberg" because it changes its nature twice on its course of dissociation (14,15). It is surprising that this Rydberg transition of the very simple H_2 molecule has not been investigated in matrices. According to the experience on the general behaviour of Rydberg states one would expect that the transition in comparison to the values for the free molecule is shifted by0,5-1eV to the blue and broadend so strongly in the Ne matrix that it may hardly be detected. Vibrational progressions with spacings similar to the gasphase should be characteristic for Rydberg states (4) in matrices, provided they can still be resolved.

2. Results

Ne gas containing H_2 with a partial pressure of 0,5 % has been deposited onto a LiF substrate at 5 ± 1K at a background pressure of 10^{-9} torr. The transmission of the sample has been measured up to the LiF cut off using monochromatized synchrotron radiation with a resolution of 1,5Å from the storage ring DORIS in Hamburg (16). The transmission spectrum (Fig.1) shows a vibrational progression of the $B^1\Sigma_u^+$ state which is very similar to a broadend gas phase progression. The dashed curve represents a fit using the gas phase energy values (Table 1), the gas phase Franck-Condon factors (17) and a gaussian line shape for the absorption coefficient with the line width and the film thickness as free parameters. The low temperature of the matrix prevents a population of higher vibrational or rotational levels in the ground state. A comparison of the fit with the experimental curve demonstrates that the $B^1\Sigma_u^+$ progression has been obsereved up to $v' = 7$, that the maxima of the absorption bands are shifted by less than 40meV and that the Franck-Condon factors are preserved in the matrix. The fit yields a linewidth fwhm H of H = 125 ± 10meV. There is a small but systematically increasing deviation from $v' = 6$ downwards to $v' = 0$ between the two curves in fig. 1 which indicates that the vibrational spacing is smaller in the matrix. A difference of about 10meV can be estimated for the lowest vibrational levels (Table 1). The transmission of 63 % at 11.0eV which remains constant down to 10eV is attributed to light scattering in the Ne matrix.

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3. Discussion

The linewidth and the change of the vibrational spacing suggest that there is a strong coupling of this transition to the lattice despite the close correspondence of the transition energies in absorption spectra of the gas and of the condensed phases. Since the observed linewidth H is similar to the linewidth of Rydberg tranitions from guest atoms (1,3) and guest molecules (3,4,5) in matrices and since the linewidth of the $B^1\Sigma_u^+$ transition in pure H_2 and D_2 is even larger, we may assume that H is due to mainly a homogenous broadening. For a guess of the electron phonon coupling strength S and the lattice relaxation energy E_{lr} we use the expressions

$$S = H^2_{T=o} \,/\, (2{,}36\ \hbar\omega_p)^2 \qquad (1)$$

$$E_{lr} = S \cdot \hbar\omega_p \qquad (2)$$

which follow for linear coupling from a configuration coordinate model in the harmonic approcimation with a single phonon frequency $\hbar\omega_p$ (18). E_{lr} is the energy difference between the maximum in the absorption band and the zero-phonon line and it gives the relaxation energy for the rearrangement of the lattice to the new equilibrum configuration around the electronically excited molecule. The experimental linewidth yields ranges for S between $112 \geq S \geq 12$ and for E_{lr} between $560\text{meV} \geq E_{lr} \geq 180\text{meV}$ assuming $5\text{meV} \leq \hbar\omega_p \leq 15\text{meV}$. 5meV is a typical bulk phonon energy for Ne and 15meV have been calculated for a local mode for H_2 molecules in Ne (19). This estimate indicates indeed a strong electron phonon coupling causing an excitation of 10 to 100 phonons simultaneous with the electronic transition. The zero-phonon transition would be red shifted by 0,2 - 0,5 eV compared to the gas phase transition energy.

These results do not fit in some points into the generally accepted picture for Rydberg states in matrices as described in the introduction. The centers of the absorption bands show a rather small blue shift compared to the gas phase and from the linewidth it is deduced that the adiabatic transition energy corresponds even to a red shift.

Furthermore the changes in the vibrational spacings of about 10meV suggest a severe distortion compared to the usual changes in matrices of only about 1meV (20). The solvation energy of the H_2 molecules in the ground state in Ne matrix amounts after summation of the H_2-Ne potential depth (21) over 12 nearest neighbours to only 30 - 50meV. Thus the dominating contribution to the red shift of the adiabatic transition energy is due to solvation of the excited state. The energy of the $B^1\Sigma_u^+$ state in the relaxed configuration of the Ne matrix is lowered by about 0,2 to 0,5eV compared to the free molecule. The changes of vibrational spacings of the OH radical in an Ar matrix (20) and that of H_2 in Ne observed by us are of similar magnitude. For OH in Ar the changes have been attributed to the formation of a strong hydrogen bond (20). The reduced energy of the $B^1\Sigma_u^+$ state and the smaller vibrational spacing can also be explained by a considerable bonding interaction between the H_2 molecule in the $B^1\Sigma_u^+$ state and the neighbouring Ne atoms. In pure solid H_2 the $B^1\Sigma_u^+$ transition has also been observed (10) with even a red shift of the centers of the absorption bands of about 0,17eV and again a reduced vibrational spacing (Table 1). The linewidth is broader than in the matrix and nearly smears out the vibrational progression. The comparison indicates an attractive interaction of H_2 molecules in the $B^1\Sigma_u^+$ state with the surrounding in a Ne-matrix and in pure solidH_2, that is more pronounced in pure solid H_2.

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Figure caption:

Fig. 1. Solid curve: transmission of 0,5 % H_2 in solid Ne-matrix at 5 K. Dashed curve: fit with gas phase energy values and Franck-Condon factors (see text).

Table 1: Band centers and vibrational spacings for H_2 in Ne (M) to ± 0,05eV; gas phase energy values (G) for $B^1\Sigma_u^+ (v', J = 0) \leftarrow X^1\Sigma_g^+ (v = 0, J = 0)$ and estimated band centers (S) for pure solid H_2 .Energies in eV.

v'	M		G[a)]		S[b)]
0	(11.22)		11.183		11.05
		0.15		0.163	
1	11.37		11.347		11.20
		0.15		0.158	
2	11.52		11.505		11.34
		0.15		0.155	
3	11.67		11.660		11.48
		0.15		0.150	
4	11.82		11.810		11.62
		0.14		0.147	
5	11.96		11.957		11.75
		0.14		0.142	
6	12.10		12.099		
		0.13		0.138	
7	12.23		12.237		

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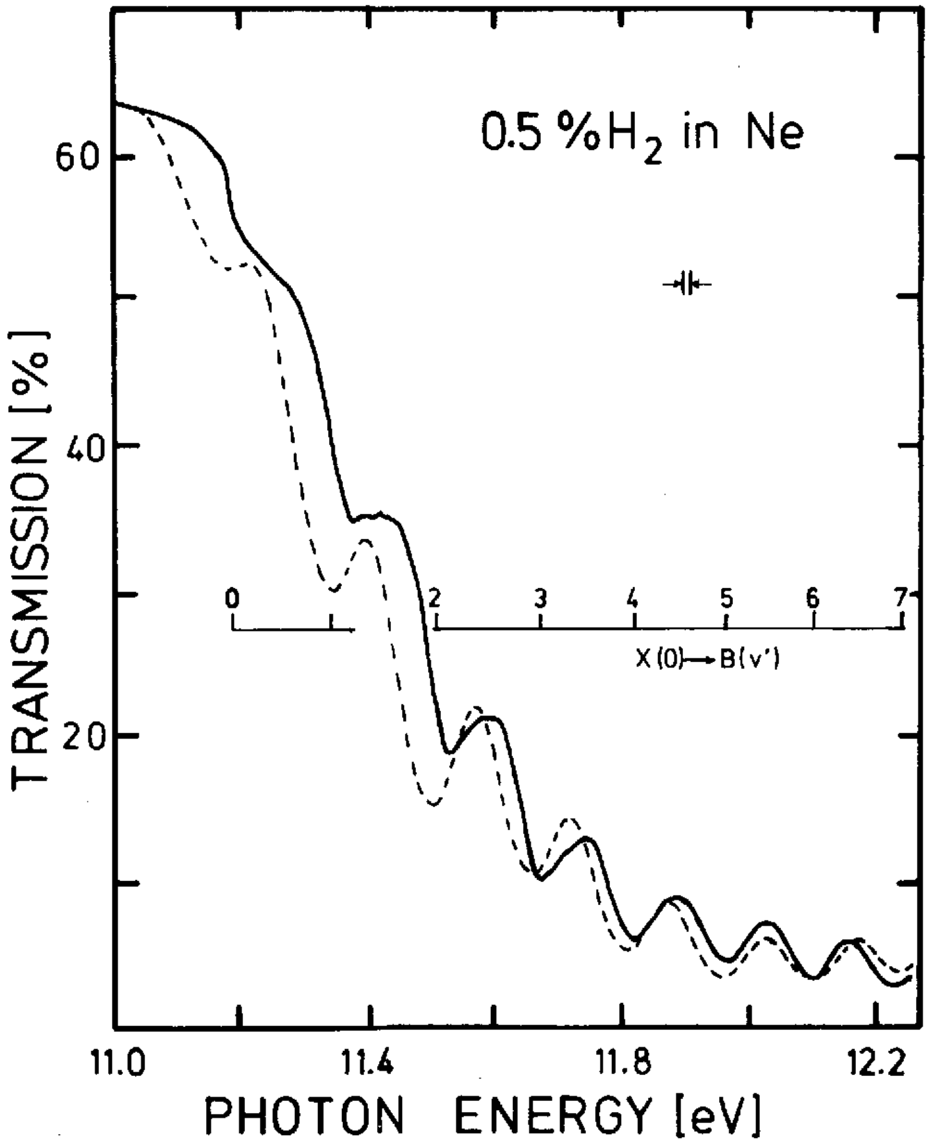

0.5 %H_2 in Ne
60
40
20
TRANSMISSION [%]
0
2
3
4
5
6
7
X(0)→B(v')
11.0
11.4
11.8
12.2
PHOTON ENERGY [eV]