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Abstract

H atoms have been stabilized in solid Ne matrices by photolysis of H_2 molecules. Photoexcitation results in the emission of L_α and L_β. The excitation spectrum of the L_α line shows maxima at 10.69 eV, 13.51 eV and 14.17 eV. The two lower energetic bands are attributed to the n = 1 and n = 2 members of a series of exciton states of the H impurity. The third maximum is tentatively assigned to predissociation of the H_2 molecules leading to an excited H atom in the 2p state and subsequent decay by L_α emission.

1) Introduction

In large bandgap insulators like solid rare gases the onset of electronic absorption is characterized by a series of exciton bands [1] . A recent discussion for the case of Ne is given in ref. [2] . The higher exciton states ($n \geq 2$) form a hydrogen like series.They are well described by the Wannier-Mott exciton model [3] which is based on the effective mass approximation. To include the n = 1 excitons, which have radii smaller than the unit cell, a central cell correction [4] has been introduced which accounts for the space dependence of the dielectric constant $\varepsilon(r)$ and of the reduced effective mass $\mu(r)$ in the unit cell. Exploiting the confinement of the electron and hole to the same unit cell the energies of the Ne n = 1 excitons have

been calculated from a superposition of molecular potential curves [5] . In several papers Resca, Resta and Rodriguez [6] tried a common description for all exciton states by the concept of a quantum defect δ . δ includes $\varepsilon(r)$, $\mu(r)$ and deviations from the Coulomb potential within a sphere around the central atoms.

The onset of absorption of Xe, Kr and Ar guest atoms in a solid Ne matrix shows also series of exciton bands [7, 8, 9] with term values for $n \geq 2$ which are very similar for the different guest atoms and also very similar to the matrix term values.

In the Wannier model differences of the term values for $n \geq 2$ can only be attributed to different reduced effective masses because the effective Rydberg constant B_W^i follows from

$$B_W^i = \frac{\mu e^4}{2\hbar^2 \varepsilon^2} \qquad 1)$$

where ε is determined by the matrix. The effective hole masses at the localized guest atoms are infinite and for pure Ne the effective hole mass $m_h \approx 20$ is very large compared to the effective electron mass $m_e = 0.802$ [10] . Therefore the differences in the reduced effective masses and in the term values for $n \geq 2$ excitons of the Ne matrix and of the guest atoms should be only 3 %. For the n = 1 excitons a central cell correction ΔE^i has to be introduced.

In the quantum defect model [11] the effective Rydberg constant B_Q^i is derived in a similar way. Differences in term values can be attributed to different quantum defects δ^i. As an important advantage the n = 1 excitons can be included in the series. In this paper we present for the first time the excitation energies of the lower exciton bands for H atoms in solid Ne matrix. Hydrogen as a guest atom is the ideal probe to test the validity of the quantum defect model because the potential of the bare H atom is of pure Coulomb-form for all distances. The origin of a quantum defect can be only the space dependence of $\varepsilon(r)$ and $\mu(r)$. Only Ne with its large band gap of 21.58 eV can be used for these investigations. Even in Ar the exciton states $n \geq 2$ of the H guest atom are covered by the absorption of the matrix itself [12] .

Furthermore we present the emission bands of H atoms in the Ne matrix. For Xe, Kr and Ar atoms the energies of the emission bands are situated between the free atom emission bands and the blue shifted absorption bands [9] . This observation has been explained by the formation of a bubble around the excited guest atom. It is interesting to see if this is a general trend supported also by results for H atoms in Ne.

Finally the preparation of H atoms by photolysis of H_2 yields some information about the dissociation processes of H_2 molecules in solid matrices.

2) Experimental

The experiments have been performed using the synchrotron radiation from the storage ring DORIS in Hamburg. Since the setup has been already described [13] we just recall that the synchrotron radiation is monochromatized by a one meter normal incidence monochromator. The low intensity in the hydrogen emission required a band pass of 5 Å. The excitation light is focused onto the sample. The emitted light is analysed by a 0.3 m Seya Namioka monochromator with a bandwidth of 20 Å again because of low intensity. The light has been detected with an open microchannel plate and alternatively with a Valvo 56 DUVP photomultiplier with sodium salicylate converter. The entire setup is operated under ultra high vacuum conditions at a background pressure of 10^{-9} torr.

Ne (purity: 99.997 %) has been mixed with H_2 (purity 99.99 %) in an ultrahigh vacuum gas handling cell. The samples have been deposited as thin films on a liquid He flow cryostat at about 5 K.

3) Results

Fig. 1 shows an emission spectrum obtained by excitation with the "white light" from the primary monochromator in zeroth order, corrected for the efficiency of the microchannel plate. The spectrum is typical for an emission spectrum after illumination of the fresh sample with "white light" for some minutes. The white light spectrum extends from 400 Å to 3000 Å and contains about 10^{12} to 10^{13} photons/sec in the region from 400 Å to 1000 Å. The increase in intensity above 13 eV in Fig. 1 is due to the long wavelength tail of the emission of pure solid Ne and the increase at low energies due to the second order contribution of the Ne emission bands. The intensity of the Ne emission bands is about 10 times that of the guest atom. From a comparison with spectra from Ne matrices doped with N_2, O_2 and CO the parasitic emission bands of these impurities in the H doped sample have been identified (Fig. 1, table 1). The emission bands of N and O atoms have also been observed after X-ray excitation of large doped Ne crystals[14]. Fig. 1 shows the L_α and L_β emission lines of H atoms. Within the experimental accuracy (± 0.05 eV) the energy of these bands in the Ne matrix is the same as in the free atom. The relative intensities of the H bands and the parasitic bands changed from sample to sample. Sometimes the L_β line has been covered by the CO impurity band at 11.9 eV. Also the emission intensity of Xe, Kr and Ar guest atoms in Ne matrix is much stronger than that of H guest atoms under similar experimental conditions. Therefore, the background of the parasitic bands appears relatively strong. Molecular H_2 emission bands could not be identified.

The L_α excitation spectrum consists of three maxima A, B, C which are listed in table 2 and a shoulder at 10.88 eV. The three maxima had approximately equal intensity. The halfwidth (0,5 eV) of maximum C was larger than that of maximum A and B (0.16 - 0.26 eV). The energy positions of these maxima do not fit in a simple way to the excited states of the free H atom. The shift of maximum A to the corresponding line L_α in the free atom is 0.49 eV and the shift of maximum B to L_β is 1.43 eV (table 2). Compared to the binding energy of L_β of 1.52 eV we observed a tremendous shift, which will be discussed in the following.

4) Discussion

4.1 Preparation of H atoms in Ne matrix

The preparation of H doped Ne samples by a deposition of a gaseous mixture of Ne with H atoms (produced by a discharge) failed [7, 15] even at sample temperatures as low as 2 K [16]. Foner et al. [16] prepared H atoms in a Ne matrix by UV photolysis of HI in Ne at 4.2 K. Our results show that it is also possible to prepare H atoms in Ne matrix by photolysis of H_2 molecules in the Ne matrix.

In the fcc lattice of solid rare gases a H atom can occupy a substitutional site or alternatively interstitial sites of D_2, D_3, T_d and O_h symmetry. Among the interstitial sites the site with O_h symmetry would be favourable. It would have a binding energy of 0.24 eV according to a calculation of the energy profile along 2 ways in the unit cell [15]. ESR experiments showed that in Ne only one kind of trapping sites is occupied by H atoms [16]. The ESR results alone do not allow to distinguish between the sites but a comparison with calculations [17, 18] suggests that the only stable trapping site in Ne is the substitutional site.

4.2 Excitation spectrum of L_α

We expect a close similarity between excitation and absorption spectra of the dopands below the absorption threshold of the matrix because the finite film thickness and the low concentration yield complete absorption of the penetrating light only for high absorption coefficients. In the samples essentially H_2 molecules and H atoms are present. Two channels are expected to contribute to the excitation spectrum.

Channel I involves excitation of an isolated H atom from 1s to 2p or to higher ecited states if necessary relaxation to the 2p state and radiative decay by L_α emission,

$$H(1s) + h\nu \longrightarrow H^{**} \longrightarrow H^{*}\ (2p, 2s) \longrightarrow H(1s) + L_\alpha$$

Channel II involves exitation of a H_2 molecule above the threshold for predissociation, dissociation to one hydrogen atom in the ground state and one in the 2s or 2p state and subsequent decay by L_α emission.

$$H_2 + h\nu \longrightarrow H_2^{*} \longrightarrow H(1s) + H^{*}\ (2p,\ 2s) \longrightarrow H(1s) + H(1s) + L_\alpha$$

The dissociation limit for decay into H(1s) + H(2s) amounts to 14.68 eV in the free molecule. Therefore, this process can be excluded for maximum A and B (table 2). Even the energy of C is smaller, but we will give some arguments in the following, that channel II is responsible for the maximum. Predissociation to higher excited states is impossible because of our restriction to energies below 16 eV.

A third channel which also involves excitation of H_2 molecules in the first step but then electronic energy transfer to an isolated H atom seems to be unimportant. The excitation spectrum has essentially no resemblance to the absorption spectrum of the free molecule [19] or of solid H_2 [20]. Absorption spectra of H_2 in Ne have not been published and the absorption spectra of D_2 in Ne [7, 21] are not conclusive in the important range of 10 eV to 14 eV. The efficiency of energy transfer is presumable small due to the competition of a fast relaxation in the dense manifold of molecular state to energies below L_α. Also a fourth channel involving excitation of the parasitic impurities N_2, O_2, CO, N, O and energy transfer to H atoms is unimportant due to the small concentration which causes a large separation and consequently a low efficiency of this process. This conclusion is supported by a comparison with the excitation spectra for the impurity emissions.

Maxima A and B

For A and B only channel I is active. In this case the intensity in the excitation spectrum is proportional to

- the number of photons absorbed at H atoms times the probability that
- the primarily excited electronic state relaxes to the 2p state, times the probability that
- the 2p state decays radiatively to the ground state.

Structures in the excitation spectrum appear only for a significant absorption coefficient and therefore maxima A and B are attributed to the lowest absorption bands, i.e. n = 1 and n = 2 excitons of H atoms in the Ne matrix. Several models to describe exciton states have been proposed.

Boursey et al. used molecular pair potentials to calculate excitation energies in molecular crystals [5] . For excitations localized at a guest atom in a matrix the excitation energy follows from the free atom energy plus the differences in the repulsive overlap and the attractive Van der Waals interaction for the ground state and the excited state. The differences are multiplied by the lattice sums [5] . The energies are taken for the equilibrium distance r_o, which will be $r_o = 3.156$ Å for a H atom in a substitutional site in the Ne matrix. The ground state potential of Ne - H(1s) shows only a very shallow Van der Waals minimum around 3.5 Å with a depth of only 1.5×10^{-3} eV and it is essentially zero at r_o [22] . Therefore, the contribution of the ground state to the excitation energies can be neglected in view of the experimental blue shift of 0.49 eV. The lowest excited states [23] are $A^2\Sigma^+$ and $B^2\Pi$ corresponding to Ne - H(2p). The next higher is the $C^2\Sigma^+$ state corresponding to Ne - H(2s). For dipole allowed transitions the H(2p) states are essential. In the cubic field of the matrix (O_h) the 2p state will not be splitted like in the $D_{\infty h}$ symmetry of the NeH* molecules. The energy of the H* (2p) state can be represented by $\frac{1}{3} A^2\Sigma^+ + \frac{2}{3} B^2\Pi$ [5] . The calculated potentials curves for $A^2\Sigma^+$ and $B^2\Pi$ are nearly degenerate [23] . They have been reported only in the range 0.8 Å < r < 2.5 Å but they seem to be purely attractive from infinity down to internuclear distances of 1 Å. From these potential curves only a red shift of the excitation energy but not be observed blue shift can be derived. The potential curves for Ne-H* show the same general features as those for He - H* [24], He_2 - H^+ [25], Ne - H^+ [26] and Ar_n - H*[27].

In these calculations repulsive barriers have been only reported for the $C^2\Sigma^+$ state but not for the $A^2\Sigma^+$ and $B^2\Pi$ states. The approximation of pairwise additivity of potential curves for excited states is the basis of the model of Boursey et al. It is in disagreement with a comparison of the potential curves for Ar - H* and Ar_2 - H* [27] in the bonding part of the $A^2\Sigma^+$, $B^2\Pi$ and $C^2\Sigma^+$ states. For the repulsive part of the $C^2\Sigma^+$ state only a few values are reported for the interesting region of r > 2 Å.

The effective mass approximation remains to explain the energy of the n = 1 and n = 2 exciton. We would like to suggest a calculation of the quantum defect from the free H atom energies using the effective Rydberg constant as has been demonstrated for the excitons of pure solid Ne by Resta [6] , because for H no free parameters enter in the calculation. Since such a calculation is missing we use the Wannier model and the quantum defect model to extract the band gap, the central cell correction or quantum defect for hydrogen in Ne. For the effective Rydberg constants B_W^i (Wannier model) and B_Q^i (quantum defect model) we take the values B_W and B_Q for pure Ne, because the differences should be only 3 % as has been explained in the introduction. This small difference is beyond the accuracy of the available experimental values. We believe that the reported scattering in B^i values [11] for Xe, Kr and Ar guest atoms is not significant but due to the few members of the series and the limited accuracy and reproducibility in excitation energies [7, 8, 9] . The data for H, Xe, Kr and Ar guest atoms are evaluated in the same way.

Wannier model

In the Wannier model the excitation energies E_n^i and the band gaps E_G^i for n > 2 simply follow by adding the values $E_n - E_2$ of pure Ne to the excitation energies E_2^i of the n = 2 exciton of the impurity. The central cell correction ΔE^i is given by

$$\Delta E^i = E_1^i + B_W^i - E_G^i$$

Quantum defect model

In this model δ^i is determined from

$$E_2^i - E_1^i = B_Q^i \left((2+\delta^i)^{-2} - (1+\delta)^{-2} \right)$$

With δ^i and E_1^i all other excitation energies E_n^i and the bands gaps can be calculated. We prefer this kind of evaluation instead of the fit procedure of ref. [11] , because the assignment of the higher exciton states is ambigious. Some exciton states belong to s and d transitions [9] and some structures remain unidentified. A comparison with the experimental values shows, that no significant differences for the predictions of both models can be derived as long as more accurate data are missing. The discrepancies to ref. [11] are mainly caused by the different sets of experimental data. E_G^i values obtained from a similar fit like in [11] but with the data of [9] would differ only by 0.1 to 0.2 eV from that of table 3. The recent data of [9] which have been used here (table 3) show more structure and higher members of the exciton series than that of [8]. Furthermore the fit procedure in [11] leads to effective Rydberg constants B_Q^i (R_S in [11]) of the order of 10 eV which seem to be too large compared to the value for pure Ne of 6,93 eV [2].

Within the experimental uncertainties the quantum defects for H, Ar, Kr and Xe atoms in Ne matrix are rather similar and of the order of 0.3 to 0.4 eV (table 3) or 0.5 to 0.6 eV [11]. In the free atoms the quantum defects increase monotonically from 0 for H to 1 for Xe (table 3). This indicates that the quantum defect in the matrix is not a specific property of the guest atom, but due to screening effects of the matrix. Since screening by space independent ε and μ are included in the effective Rydberg constant used in the effective mass approximation, the quantum defect monitors the space dependent part. Thus the space dependent part of ε and μ is mainly due to the matrix.

From the bandgap of hydrogen in Ne also the hole polarization energy P_+ can be calculated [28] using the electron affinity V_0 = 1,4 eV of Ne [29] and the ionization energy I_g = 13,6 eV of H. The value of $P_+ = -0.2 \pm 0,5$ is surprisingly small compared to the expectation of $P_+ \approx 1.5$ eV from a simple model [30].

Maximun C

Maximum C has a smaller energy than the bandgap. Therefore, it does not correspond to the onset of continuum absorption of the H atoms. The large width and the large intensity exclude an assignment only to higher excitons $n > 2$. We suppose that maximum C is partly caused by predissociation (channel II). This requires that the onset of predissociation is reduced in the Ne matrix at least by 0.5 eV. This can be exlained by the strong attraction of Ne and H for excited H^* atoms which is evident from the deep minima in the potential curves of the $A^2\Sigma^+$, $B^2\Pi$ and $C^2\Sigma^+$ states.

4.3 Emission spectrum

In emission the free atomic L_α and L_β lines are observed. The red shift of 0.49 eV indicates a remarkable relaxation of the lattice of the Ne matrix in the surrounding of the excited H atoms. The shift to the free atom indicates that the relaxed configuration resembles more the free atom configuration. The formation of a bubble around the excited H atoms with an increased nearest neighbour separation to the Ne atoms is the appropriate explanation. The same tendency has been observed for Xe, Kr and Ar guest atoms [9, 14] .
Two aspects are surprising: First the emission of the L_α line shows that bubble centers can compete with the formation of Ne_n-H^* centers with smaller Ne-H^* nearest neighbour separation corresponding to the equilibrium distance of 1 Å of the $A^2\Sigma^+$, $B^2\Pi$ and $C^2\Sigma^+$ states. Second, if we assume that maximum C is due to predissociation then the subsequent emission of L_α requires that also the ground state energy of H in Ne is lowered by 0.5 eV. This is in contradiction to the smallness of the Van der Waals minimum of the Ne-H ground state potential [22], but agrees with the configuration model calculations for H in Ne even for an intenstitial site [15] .

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Figure captions:

Figure 1: Emission spectrum of H_2 in Ne matrix at 5 K after white light excitation (see text). The bars show energies of the free atoms.

Table 1

Emission bands of doped Ne samples [± 0,05 eV] .

	assignment	emission band eV	gas value eV a)	matrix shift eV
H	1s - 2p	10,16	10,20	-0,04
H	1s - 3p	12,10	12,08	0,02
O	$2s^22p^4-2s^22p^33s$	9,61	9,52	0,09
N	$2s^22p^3-2s^22p^23s$	10,45	10,33	0,12
N	$2s^22p^3-2s2p^4$	11,00	10,93	0,07
CO		11,70		
CO		11,90		

a) R.L. Kelly, L.J. Palumbo, N.R.L. Report 7599 (1973)

Table 3

Bandgaps E_G, E_G^i, central cell corrections ΔE, ΔE^i, quantum defects δ , δ^i in the Wannier model (W.M.) and quantum defect model (Q.M.) for a Ne matrix. In the calculations the effective Rydberg constants (B_W, B_Q) of the Ne matrix have been used: $B_W^i = B_W = 5.00$ eV; $B_Q = B_Q^i = 6.93$ eV (a). δ_A: quantum defect of free atom. (b)

	Ne 3/2	H/Ne		Ar/Ne 3/2		Kr/Ne 3/2		Xe/Ne 3/2	
		W.M.	Q.M.	W.M.	Q.M.	W.M.	Q.M.	W.M.	Q.M.
E_G, E_G^i	21.58	14.76	14.85	16.09	16.04	14.57	14.64	12.57	12.51
δ , δ^i	0.28		0.29		0.40		0.31		0.43
δ_A	0.67-0.70		0		0.81-0.87		0.85-0.92		0.92-0.99
ΔE, ΔE^i		0,93		1.39		1.03		1.53	

a)Ref. 2

b)C.E. Moore Atomic Energy Levels, Natl.Bur.Circ.No 467 (U.S. 680 Washington D.C. 1958)

Table 2

Excitation energies of the L_α emission band of H in Ne ($\pm$ 0,05 eV)

	excitation energy [eV]	free atom [eV]		matrix shift [eV]
A	10,69	L_α	10,20	0,49
B	13,51	L_β	12,08	1,43
C	14,17	L_γ	12,75	1.42

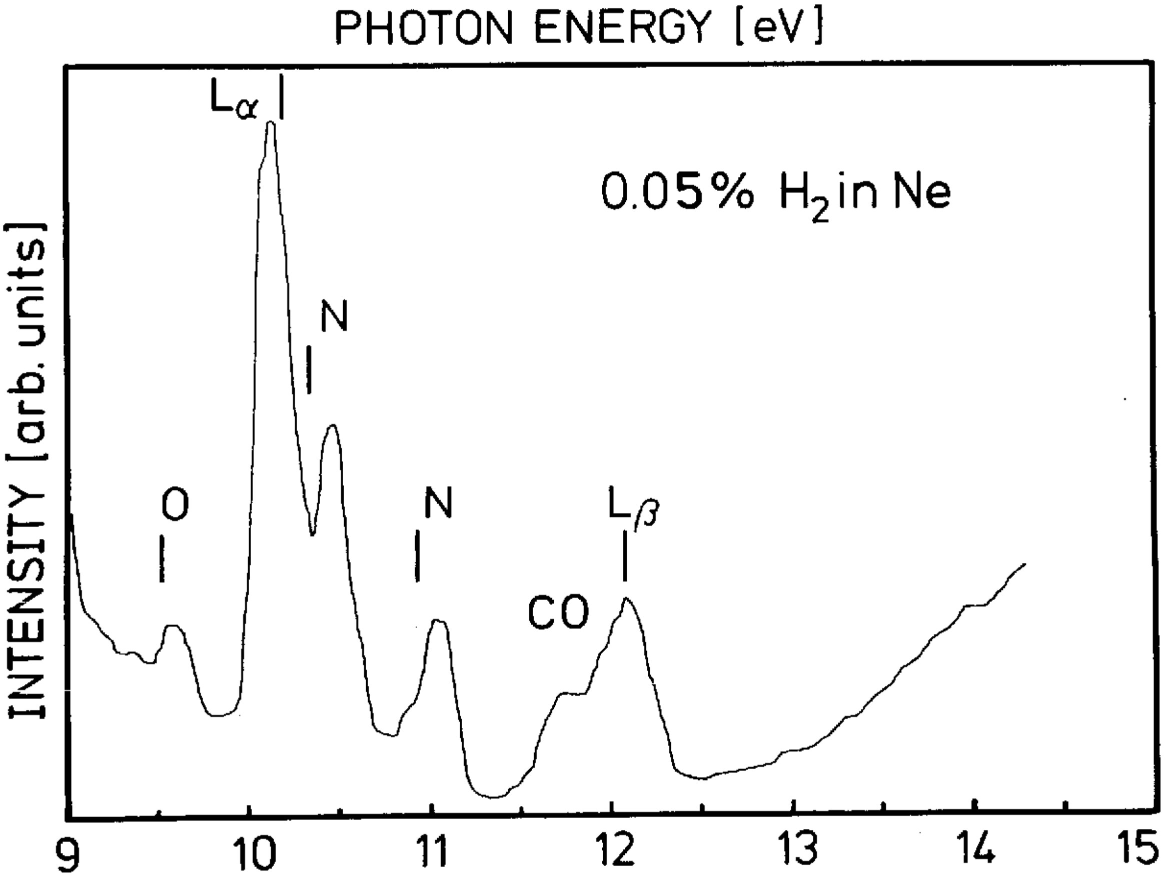
PHOTON ENERGY [eV]
INTENSITY [arb. units]
0.05% H_2 in Ne
L_α
N
O
N
CO
L_β
9
10
11
12
13
14
15

Fig. 1