

RYDBERG SERIES OF CHARGE TRANSFER EXCITATIONS IN HALOGEN-DOPED RARE GAS CRYSTALS

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Charge transfer excitations of halogen-doped rare gas solids are treated as Rydberg progressions of hole states. The analysis is in good agreement with experiments performed in Cl-, Br- and I-doped xenon.

Recently Fajardo and Apkarian [1] recognized that the optically accessed charge transfer states of solid xenon doped with atomic halogens are excitonic in nature: an electron of infinite effective mass localized on the halogen atom and a delocalized hole in the extended solid which is bound to the negative center via a screened Coulombic potential. The description is analogous to that of excited Rydberg states of alkali atoms isolated in rare gas matrices (with the obvious inversion of signs of charges), an analysis of which was recently given by Schwentner and Chergui [2]. In this communication, we present an interpretation of the observed charge transfer excitation spectra of halogens in xenon in the Rydberg framework and discuss the expected series in the lighter rare gases.

The treatment of excitons in the framework of Frenkel- and Wannier-type states and the conditions for applying the effective mass approximation are well established [3,4]. Rare gas crystals show prominent progressions of excitons [5,6], which have been discussed in detail as being intermediate between Frenkel (for $n=1$) and Wannier (for $n \geq 2$) excitons. Hydrogenic progressions in the excited states of heavier rare gas atoms doped in lighter rare gas matrices, have been attributed to bound excitonic states in which the hole is localized at the dopant with an infinite effective mass, $1/M_h = 0$ [6-9]. The

electron wavefunction is then derived from the host conduction band and accounted for by an electron effective mass, M_c . The Coulombic interaction between the electron and the positive ionic core is shielded by the host dielectric. A Rydberg series with main quantum number n and which converges to the bottom of the host conduction band is expected in this scheme. For sufficiently large electron orbits, characterized by radii r_n , the use of the continuum dielectric constant, ϵ , for the shielded potential is justified. In this effective mass approximation, the term values, B_n , and radii, r_n , of the Rydberg states are given by

$$B_n = 13.6\mu/\epsilon^2 n^2 \text{ (eV)}, \quad (1)$$

$$r_n = n^2 \epsilon a_0 / \mu \text{ (\AA)}, \quad (2)$$

in which

$$1/\mu = 1/M_c + 1/M_h. \quad (3)$$

While the more common situation encountered in doped insulators is that of an electron orbiting a positively charged ion core the formulation of eqs. (1)–(3) should apply as well to the case of a hole orbiting a negatively charged ion core. In the latter case a Rydberg series of excited hole states is to be expected. To the best of our knowledge, such progressions of excited hole states in typical insulators – such

as alkali halide, rare gas, or molecular crystals – have not been discussed in the literature to date. The closest parallel is that of doped semiconductors. The ionization energies of donors in the band gap of semiconductors are estimated by the first term value, B_1 , of eq. (1) with $\mu = M_e$ [10,11]. The corresponding energies of acceptors above the valence band of semiconductors are deduced in analogy replacing μ by M_h in eq. (1). A progression of hole states is to be expected by creating deep acceptor levels in the band gap – a condition satisfied in the case of rare gas crystals when doped with halogen atoms which have large electron affinities. Charge transfer in this case creates a negatively charged halogen, X^- , and a hole in the valence band of the solid. The analogy to ionization is the creation of a delocalized free hole, R^+ . The Rydberg series of these charge transfer states correspond to excited states, R^* , in which the hole remains bound in the Coulombic field of the spatially fixed negatively charged halogen atom. The hydrogenic progression of hole states should converge to the top of the rare gas valence band. Since the negative charge is localized, $1/M_e = 0$. The effective reduced mass in eq. (3) is then given by the effective hole mass, M_h , at the top of the rare gas valence bands.

The relevant parameters to calculate the term values and radii from eqs. (1) and (2) are collected in table 1. M_h has been derived from the M_e and μ values presented by Rössler [5]. There has been concern about the accuracy of Rössler's band structure calculations, since both experiments [15,16] and other calculations [5] have yielded broader valence bands implying smaller effective hole masses. The $\Gamma_8^- - L_6^-$ splitting and the $\Gamma_8^- - X_6^-$ splitting according

Table 1
Electron effective mass M_e and reduced effective mass μ (from table 3 in ref. [5]) used to derive the hole effective mass M_h , together with dielectric constant ϵ [5]

	Ref.	M_e	μ	M_h	ϵ
Ne	Kunz [12]	0.802	0.78	28.4	1.24
Ar	Rössler [13]	0.48	0.44	5.3	1.66
	Kunz [12]	0.488	0.45	5.8	
Kr	Rössler [13]	0.42	0.35	2.1	1.86
	Kunz [12]	0.418	0.36	2.6	
Xe	Rössler [13]	0.35	0.30	2.1	2.18
	Reilly [14]	0.51	0.40	1.90	

to Rössler's calculated values are 0.7 and 0.82 eV, respectively [5]. While the most recent experimental value for the $\Gamma_8^- - L_6^-$ splitting in bulk xenon is 0.97 eV [11]. Despite such discrepancies, we have chosen Rössler's calculated values since they represent a consistent set of band structures for Ar, Kr, and Xe.

The potential acting at the hole in the region of the X^- core, i.e. at distances smaller than the nearest neighbor separation, is expected to deviate from the Coulomb potential. The influence of the core potential can be accounted for by introducing an effective main quantum number n^* in eqs. (1) and (2) in analogy to the treatment of Rydberg states in the gas phase [17]. This concept has been applied for excited states of pure gases and of rare gas atoms in rare gas matrices [6,18,19]. Recently it has been used to explain the observed s-p splitting and the higher members or Rydberg states of alkali metal atoms in rare gas matrices by combining an appropriate potential with the gas phase n^* values [2]. The gas phase $n\sigma$, $n\rho\sigma$ and $n\rho\pi$ splitting in NO for $n=3$ and 4 is also observed in rare gas matrices [20]. Both examples indicate that the lifting of the orbital degeneracy due to the core is also a very essential feature of Rydberg progressions in the condensed phase. Despite the problems of the quantum defect models discussed in the literature it seems tempting to apply as a first attempt the gas phase n^* values also to the matrix-isolated species.

A negatively charged halogen is a closed-shell system and corresponds to the core of an alkali atom in the next row of the periodic system with only the sign of the charge inverted. Thus the hole orbiting around X^- is analogous to an alkali atom and the relevant n^* values are those of the corresponding alkali atom. The n^* values and their associated term values B_n^c , calculated from eq. (1), are collected in table 2 for Cl^- , Br^- and I^- in solid Xe. The experimental term values B_n , obtained from ref. [1], are also included in table 2. The effective mass approximation is restricted to states with an orbit r_n at least as large as the nearest neighbor separation. B_n^c values of states with smaller r_n values (see table 3) are given in parentheses in table 2. These term values are meaningless because the states within the core experience a significant central cell correction, a subject beyond the scope of this paper.

Table 2

Calculated term values B_n^c compared with experimental term values B_n [1] (in eV) in Xe matrix. For n^* of Cl^- , Br^- , and I^- the values for K, Rb and Cs have been taken

	Cl^-			Br^-			I^-		
	n^*	B_n^c	B_n	n^*	B_n^c	B_n	n^*	B_n^c	B_n
4S	1.770	(1.92)							
4P	2.234	(1.20)							
5S	2.801	0.76	0.72	1.805	(1.84)				
5P	3.265	0.56	0.54	2.280	(1.15)				
6S	3.810	0.41	0.41	2.845	0.74	0.73	1.869	(1.72)	
6P	4.275	0.33		3.317	0.54	0.53	2.329	(1.11)	
7S	4.814	0.26		3.856	0.40	0.40	2.920	0.70	0.73
7P	5.280	0.22		4.329	0.32		3.374	0.53	0.54
8S				4.861	0.25	0.22	3.934	0.39	0.40
8P				5.335	0.21		4.389	0.31	0.32
9S							4.940	0.25	0.22
9P							5.396	0.21	

The agreement of the predicted term with the observed ones is quite stimulating (table 2). The discrepancies are smaller than 0.04 eV, which is surprisingly good. The experimental term values have been derived from excitation spectra by monitoring the intensity in a strong luminescence band in well-annealed samples [1]. The luminescence is due to the decay of $\text{Xe}_2^+ \text{X}^-$ charge transfer states to the

neutral ground state. These excitation spectra are similar to absorption spectra and are reproduced in fig. 1. The broad continuum to the right-hand side has been attributed to the charge transfer excitation continuum leading to X^- and a free hole R^+ [1]. The ionization energies C_0 given by the thresholds follow quite well the expected relation

$$C_0 = \text{IP} - \text{EA} + P^+ - P^- \quad (4)$$

Table 3

Calculated term values B_n^c and exciton radii r_n compared with experimental term values B_n (in eV) and successive radii a_n (in Å) of shells in a fcc lattice for I^- in Ne, Ar, Kr and Xe matrices. n.o. means no progressions observed

		6S	6P	7S	7P	8S	8P	9S	9P
Ne	B_n^c	71.9	46.3	29.4	22.0	16.2	13.0	10.3	8.62
	B_n	n.o.							
	r_n	0.07	0.11	0.17	0.23	0.30	0.39	0.49	0.58
Ar	B_n^c	7.5	4.83	3.07	2.30	1.69	1.36	1.07	0.90
	B_n	n.o.							
	r_n	0.59	0.92	1.45	1.94	2.63	3.27	4.15	4.95
	a_n							3.755	
Kr	B_n^c	2.36	1.52	0.97	0.73	0.53	0.43	0.34	0.28
	B_n	n.o.							
	r_n	1.64	2.55	4.01	5.35	7.27	9.05	11.47	13.68
	a_n			3.992	5.646	6.914	7.984	8.927	
Xe	B_n^c	1.72	1.11	0.70	0.53	0.39	0.31	0.25	0.21
	B_n			0.73	0.54	0.40	0.32	0.22	
	r_n	1.92	2.98	4.69	6.26	8.51	10.59	13.42	16.01
	a_n			4.340	6.138	7.517	8.680	9.705	

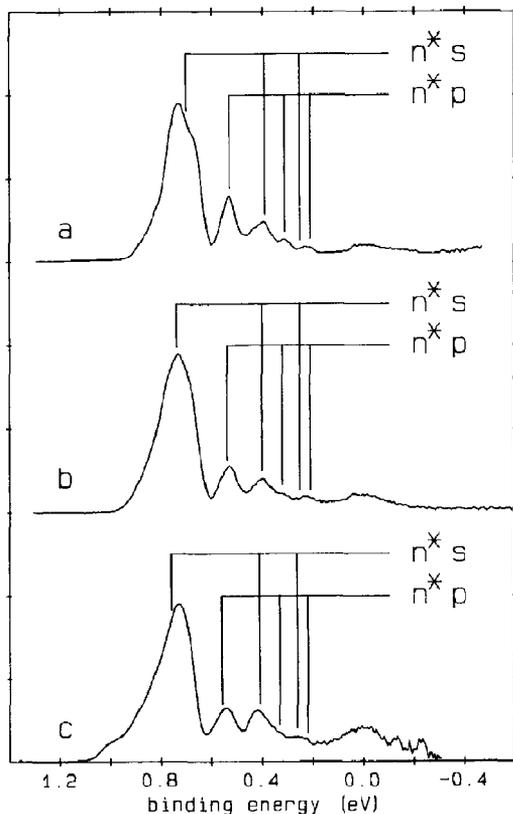


Fig. 1. Experimental charge transfer excitation spectra of I-, Br-, and Cl-doped xenon taken from ref. [1] are shown in (a), (b) and (c). The abscissa corresponds to the binding energy of the hole. The spectra are shifted to match a common origin which is lined up with the broad feature assigned to the creation of a free hole. The indicated lines correspond to term values of the first three members in s and p progressions. The term values and effective quantum numbers are collected in table 2.

within the error limits of the polarization energies P^+ and P^- of the hole and the negative charge, respectively [1]. IP is the gas phase ionization energy of Xe and EA the electron affinity of the particular halogen. P^+ and P^- are the self energies of the hole and negative ion as discussed in ref. [1]. The ionization thresholds in fig. 1 have been placed at zero energy for comparison. The structures below the continuum represent the bound states of the Xe^+ hole. They have to be compared with the calculated term values, which are given by the stick pattern. Fig. 1 demonstrates that the agreement is really encouraging and the discrepancies are only of the order of

the accuracy of the reading of the peak position. In view of the uncertainties in the hole masses and the assumptions involved in using n^* the agreement seems perhaps to be somewhat fortuitous. The direct excitation of the first term value from the ground state cannot be obtained from eq. (1) alone because it includes the charge transfer to the halogen atom. Therefore eqs. (1) and (4) together are required to predict this transition energy. The situation is different in this respect from the case of alkali atoms in matrices where the ground state is already a Rydberg state.

The first strong transition in the experimental spectra of fig. 1 contains most probably the first term value with a sufficiently large r_n to fulfill the prepositions of the effective mass approximation and also the excitations within the ionic core which will be modified by a central cell correction. The intensity and the width of the transition will be enhanced by this convolution. The intensities of the higher members should go down with $(n^*)^{-3}$ in each ns and np series. The expected decrease from the second maximum to the fourth maximum would be a factor of 2.2 for XeI, which is consistent with the experimental data.

The hole orbits, r_n , are compared with radii, a_n , of successive shells in the fcc lattices of Ne, Ar, Kr and Xe crystals for an I^- dopant in table 3. The preposition of the effective mass approximations of $r_n \geq a_1$ with the nearest neighbor separations is fulfilled for Xe and Kr crystals already by the third term value, for Ar it is the seventh term value and for Ne it would be far beyond the eighth term value. Members of Rydberg progressions as high as 7 have never been observed in insulators such as rare gas crystals or alkali halides presumably because of intensity reasons, and due to broadening and merging of these resonances into the continuum. The model predicts that hole Rydberg progressions should appear in Xe, perhaps Kr but not in the lighter rare gases Ar and Ne. The favour of heavier rare gases for hole Rydberg progressions is opposite to the trend for electronic progressions. r_n is proportional to $1/\mu$ according to eq. (2). μ corresponds to the hole effective mass for hole progressions and it decreases with atomic weight. For electron progressions μ corresponds to M_e and increases with atomic weight. Therefore the r_n values of electronic progressions are largest for a given n in

Ne and the most pronounced exciton progressions have been observed in pure and doped Ne. For hole progressions the r_n values are largest in Xe and it is until now the only matrix to show a hole progression. The trend derived from μ is enforced by the ϵ values. Kr could be a further matrix to sustain hole progressions.

There is an interesting accidental correlation between a_1 and a_2 and the r_n values of the first two observed term values (table 3). The hole is orbiting in the vicinity of the first or second shell of Xe atoms and the requirements of a continuum model are therefore more easily fulfilled. For the next higher r_n values several shells of atoms come into play and a continuum picture is appropriate. The correlation of r_n with the lattice structure has already been recognized in ref. [1]. There, the progressions have been explained by a distribution of static holes in the Coulomb potential of the negative charge, fixed at distances corresponding to the shell radii r_n . The predictions by this model are in similar good agreement but only if the value of the Coulomb potential is reduced by a factor of two. This observation points to an orbiting charge as has been mentioned in ref. [1]. The binding energy for an orbiting charge is just half of the potential energy due to the balance in kinetic and potential energy. Obviously the fits in ref. [1] are an independent justification of the model presented here. The problem of predicted alternating intensities due to the occupation numbers of the shells is also resolved by the present exciton model.

We hope that the success of this heuristic treatment of hole Rydberg progressions in insulators stimulates an experimental search in other charge transfer systems and leads to more profound theoretical investigations of the problem.

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References

- [1] M.E. Fajardo and V.A. Apkarian, *J. Chem. Phys.* 85 (1986) 5660; *J. Chem. Phys.* (1988), in press.
- [2] N. Schwentner and M. Chergui, *J. Chem. Phys.* 85 (1986) 3458.
- [3] R.S. Knox, *Theory of excitons* (Academic Press, New York, 1963).
- [4] M. Ueta, H. Ranzaki, K. Kobayashi, Y. Toyozawa and E. Hanamura, *Solid-state sciences*, Vol. 60. Excitonic processes in solids (Springer, Berlin, 1986).
- [5] U. Rössler, in: *Rare gas solids*, Vol. 1, eds. M.K. Klein and J.A. Venables (Academic Press, New York, 1976) p. 505; B. Sonntag, in: *Rare gas solids*, Vol. 2, eds. M.K. Klein and J.A. Venables (Academic Press, New York, 1976) p. 1021.
- [6] N. Schwentner, E.E. Koch and J. Jortner, *Springer tracts in modern physics*, Vol. 107. Electronic excitations in condensed rare gases (Springer, Berlin, 1985).
- [7] J. Jortner, in: *Vacuum ultraviolet radiation physics*, eds. E.E. Koch, R. Haensel and C. Kunz (Vieweg-Pergamon, Braunschweig, 1974) p. 263.
- [8] D. Pudewill, F.-J. Himpfel, V. Saile, N. Schwentner, M. Skibowski, E.E. Koch and J. Jortner, *J. Chem. Phys.* 65 (1976) 5226.
- [9] J. Jortner, E.E. Koch and N. Schwentner, in: *Photophysics and photochemistry in the vacuum ultraviolet*, eds. S. McGlynn, G. Findley and R. Huebner (Reidel, Dordrecht, 1984) p. 515.
- [10] S.M. Sze, *Physics of semiconductor devices* (Wiley, New York, 1969) p. 28.
- [11] C. Kittel, *Introduction to solid state physics* (Wiley, New York, 1986) p. 206.
- [12] A.B. Kunz and D.J. Mickish, *Phys. Rev. B* 8 (1973) 779.
- [13] U. Rössler, *Phys. Stat. Sol.* 42 (1970) 345.
- [14] M.H. Reilly, *J. Phys. Chem. Solids* 28 (1967) 2067.
- [15] N. Schwentner, F.-J. Himpfel, V. Saile, M. Skibowski, W. Steinmann and E.E. Koch, *Phys. Rev. Letters* 34 (1975) 528.
- [16] K. Horn, A.M. Bradshaw, *Solid State Commun.* 30 (1979) 545.
- [17] E.U. Condon and G.H. Shortley, *The theory of atomic spectra* (Cambridge Univ. Press, Cambridge, 1959); R.F. Stebbings and R.B. Dunning, *Rydberg states of atoms and molecules* (Cambridge Univ. Press, Cambridge, 1983).
- [18] K. Dessler, *Extrait des mémoires de la Société Royale des Sciences de Liège*, Vol. 20 (Liège, 1970) p. 357.
- [19] L. Resta and S. Rodriguez, *Phys. Rev. B* 17 (1978) 3334; R. Resta, *Phys. Stat. Sol.* 86 (1978) 627; L. Resta, R. Resta and S. Rodriguez, *Phys. Rev. B* 18 (1978) 696, 702.
- [20] M. Chergui, N. Schwentner and W. Böhmer, *J. Chem. Phys.* 85 (1986) 2472.