

A priori calculation of the $n = 1$ valence exciton of solid neon

E. Boursey, M.-C. Castex, and V. Chandrasekharan

*Laboratoire des Interactions Moléculaires et des Hautes Pressions, Centre National de la Recherche Scientifique,
Centre Universitaire Paris-Nord, Avenue J.-B. Clément, 93430 Villetaneuse, France*

(Received 15 March 1977)

The energies of the $n = 1$ excitons in solid neon have been calculated on the basis of the *ab initio* repulsive-potential curves of the molecular excited states derived from 3P and 1P states of neon and the long-range Van der Waals interaction of these states. With this rigorous parameter-free calculation a very good agreement with experimental results is obtained for the first exciton doublet.

I. INTRODUCTION

Rare-gas solids are the simplest of all molecular solids and during the last decade ground-state properties have been almost completely understood.¹ Great strides have been made in the understanding of excited states but with much less success. At present the experimental features observed in the optical properties of the rare-gas solids in the fundamental excitation range have been mainly described by a band structure associated with the Wannier exciton model,² i.e., a weakly interacting electron-hole pair. The eigenvalues of the modified hydrogenic equation approximating the interaction between electron and hole can be expressed in the well-known form

$$E_n = E_G - B/n^2 \quad (1)$$

with E_G gap energy, B binding energy, and n principal quantum number. Then the observed bands form an exciton series from the valence band to the conduction band at the Γ point. However, it has been recognized from the beginning that such a model fails to describe the $n=1$ member of the Rydberg-Wannier series in rare-gas solids. For this state the exciton radius becomes so small that the charge distribution of the electron and hole overlap, in contradiction with the basic hypothesis that the pair extends over a distance large compared to the lattice constant. Allowance for core penetration can be made either by introducing a charge-transfer model as suggested by Webber *et al.*³ or by taking account of a central-cell correction increasing with exciton energy as proposed by Hermanson *et al.*⁴ With an alternative interpretation assuming the electron and hole to be confined to the same unit cell in the intermediate-coupling approximation, Andreoni *et al.* have been able to obtain good agreement for this lowest exciton in neon and argon.^{5,6} However, the Wannier scheme does not make any direct reference to the free atomic energy levels. In other respects it has been remarked by one of us⁷ (E. B.) that the

fundamental absorption spectrum of solid neon is close to the free-atom transitions $2p^6 \rightarrow 2p^5ns, n's'$. Further support for this remark comes from the analysis of the spectra of rare-gas dimers developed by Tanaka *et al.*⁸ and Castex.⁹ They have observed transitions from discrete bound states of Van der Waals dimers in the ground electronic state to excited molecular states closely related to atomic level $ns, n's'$. In the same spirit Tilton *et al.*¹⁰ have recently observed rare-gas dimer spectra in alkali-metal hosts. Cohen and Schneider^{11,12} have carried out *ab initio* calculations of the potential curves of the molecular excited states derived from 3P and 1P states of neon. Relying strongly on these calculations, we have been able to deduce directly the energies of both the $n=1$ valence bulk excitons of solid neon.

II. GENERAL FORMULATION

In molecular crystals the excitation energy E_f for transition from the ground state to the excited state f is expressed by¹³

$$E_f(K) = \Delta\epsilon_f + D_f + L_f(k), \quad (2)$$

where (i) $\Delta\epsilon_f$ is the excitation energy of the free atom,

$$(ii) D_f = \sum_m (\langle \phi_n^0 \phi_m^f | V_{mn} | \phi_m^f \phi_n^0 \rangle - \langle \phi_n^0 \phi_m^0 | V_{mn} | \phi_m^0 \phi_n^0 \rangle) \quad (3)$$

is the environmental shift in interaction energy of one excited molecule with all the surrounding molecules, (iii) $L_f(k)$ gives the resonance interaction, and (iv) V_{mn} is the Hamiltonian of the interatomic interaction which is assumed to be the sum of the repulsive overlap and Van der Waals interaction:

$$V = V_{\text{rep.}} + V_{\text{att.}} \quad (4)$$

both for the ground and the excited states.

The approximation of pairwise additivity of the potential has been extremely fruitful in describing

the ground-state potential of the crystal¹ and is assumed to hold also for the interaction of the excited molecule with the surroundings, as implied in Eq. (3). For the attractive part of the potential (C_6^f, C_8^f) of the excited states, the matrix element for an fcc lattice¹ is

$$D_f = 14.45(C_6^f - C_6^0)/R^6 + 12.80(C_8^f - C_8^0)/R^8, \quad (5)$$

where C_6 and C_8 are given by the Slater-Kirkwood relations,¹⁴

$$C_6/R^6 = -3e^2/2a_0 \frac{\alpha_0^{3/2}}{(\alpha_1/N_1)^{1/2} + (\alpha_2/N_2)^{1/2}} \frac{\alpha_1 \alpha_2}{R^6}, \quad (6)$$

where α_1 and α_2 are the polarizabilities of the two interacting atoms, N_1 and N_2 are the number of outer-shell electrons, a_0 is the Bohr radius, and the polarizabilities are deduced from the usual dispersion relation¹¹

$$\alpha_i = h^2 e^4 a_0 \sum_j f_{ij} / (E_i - E_j)^2,$$

where f_{ij} are experimental oscillator strengths for the transition i to j . For the ground-state atom (0) $N_1 = 6$ and, for the excited-state atom (f) $N_2 = 1$ were used and

$$C_8/R^8 = -\frac{45}{4}(e^2/2a_0)\alpha_0^2 \times \left\{ \frac{1}{1 + 2(\alpha_1 N_2/N_1 \alpha_2)^{1/2}} + \frac{1}{1 + 2(\alpha_2 N_1/N_2 \alpha_1)^{1/2}} \right\} \frac{\alpha_1 \alpha_2}{R^8}. \quad (7)$$

R is the nearest-neighbor distance, and the coefficients in Eq. (5) arise from the lattice sums.¹

In order to calculate the repulsive interaction we have to briefly indicate the correlation¹⁵ between the monomer, dimer, and exciton states as shown schematically in Fig. 1 with particular reference to neon. In the atom only transitions to 3P_1 and 1P_1 are allowed. The 3P_1 (or 1P_1) state is correlated to the F_{1u} state in the crystal which is not split in the crystalline field of symmetry O_h and remains single as there is only one atom per unit cell. However, in the molecule of symmetry $D_{\infty h}$ the anisotropic forces split it into 0^+ and 1 states and, furthermore, as there are two atoms per molecule, there are twice as many states $0_u^+, 1_u, 0_g^+$, and 1_g . Thus, in the crystal with only one atom per unit cell half these states (0_g^+ and 1_g) disappear. It is important to emphasize that at the Γ point the excited state $|f\rangle = N^{-1/2} \sum_n \psi_n^f$ has the symmetry u and not g just as, for example, the molecular state u is given by

$$1/\sqrt{2} \{ (^1S_a)(^3P_b) + (^1S_b)(^3P_a) \},$$

where a, b represent the two atoms and hence the

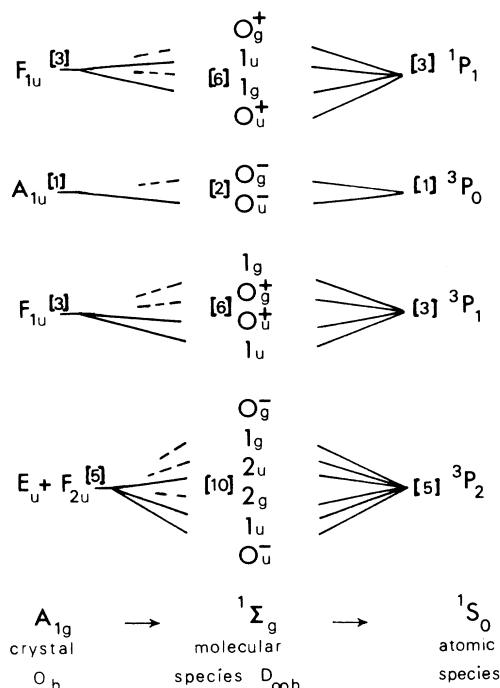


FIG. 1. Schematic correlation between monomer, dimer, and exciton states. (a) Dotted lines indicate levels which have no correlated states in the crystalline symmetry. (b) Brackets indicate the state degeneracy. (c) Ordering of molecular states is deduced from Ref. 11 at nearest-neighbor distance R in the solid.

u states of the molecule and crystal are correlated. As the crystal is isotropic we make use of the relation

$$F_{1u} = \frac{1}{3}0_u^+ + \frac{2}{3}1_u. \quad (8)$$

This enables us to extract the repulsive interaction for the excited state from the results of Cohen *et al.*,^{11,12} at R equal to the nearest-neighbor distance. It should be remarked that in their *ab initio* calculations, Cohen *et al.* do not include the long-range part of the potential energy interaction which they calculate¹¹ separately using Eq. (6). For the repulsive part of the ground state we have taken the results of Farrar *et al.*¹⁶ deduced from elastic differential cross-section measurements of molecular beams. Since the repulsive potential falls very rapidly, the matrix element of this part is taken to be 12 times that of the simple molecule.

The resonance interaction term depends on the wave vector of the excited state and gives rise to splitting into longitudinal and transverse excitons. This leads to the additional terms^{17,18}

$$L_f^\perp = -\frac{1}{3}(\epsilon + 2)(4\pi d^2 \sqrt{2}/3R^3) \quad (9)$$

and

TABLE I. Individual and weighted values of the repulsive potential of the excited states of Ne₂. All entries in eV.

0_u^* (3P_1)	0.117 ^a	F_{1u}	0.115 ^b
1_u (3P_1)	0.114 ^a		
1_u (3P_2)	0.087 ^a	F_{2u}	0.086 ^b
0_u^- (3P_2)	0.083 ^a		
0_u^* (1P_1)	0.064 ^a	F_{1u}	0.116 ^b
1_u (1P_1)	0.143 ^a		

^aDeduced from Ref. 11 using fundamental constants of Ref. 1, R being taken equal to 5.964-a.u. nearest-neighbor distance in solid neon.

^bIsotropic average $F_{1u} = \frac{1}{3} 0_u + \frac{2}{3} 1_u$.

$$L_f'' = \left(\frac{\epsilon + 2}{3\epsilon} \right) \frac{8\pi d^2 \sqrt{2}}{3R^3} \quad (10)$$

for finite k , where d is the transition dipole moment given by

$$d^2 = \frac{e^2 h f}{8\pi^2 m \nu} \quad (11)$$

and f the oscillator strength of the transition with frequency ν . The dielectric constant ϵ in these equation takes into account not only its shielding effect but also the amplification of the interaction of two polarizable atoms. Since only the transverse exciton is observed in absorption,¹³ only the first term (9) is taken into account. In the molecule, this resonance interaction gives rise to the first-order dispersion coefficient C_3/R^3 as given by Cohen *et al.*¹¹ The sum of these interactions gives the total shift $D_f + L_f^{\frac{1}{2}}$ for the electronic transitions.

III. A PRIORI CALCULATIONS FOR NEON

In Table I we present the values of the repulsive matrix element of the excited states of Ne₂ as de-

duced from the work of Cohen *et al.*¹¹ at R equal to 5,964 a.u., the nearest-neighbor distance in solid neon at 4 K. Table I exhibits also the isotropic average per neighbor for the exciton states in the crystal.

For the attractive part of the potential C_6^f of the excited state we used the isotropic part given by Cohen *et al.*^{11,19}; in addition we included also the C_8^f part.^{14,19} Then the matrix element D_f for the solid is obtained from Eq. (5). In order to calculate the resonance shift for transverse modes we used the oscillator strength in the solid given by Pudewill *et al.*²⁰ Table II summarizes the different contributions in solid neon. We compare the experimental and calculated shifts in Table III. The agreement between the theory and experiment is very good particularly when one considers that this is a completely *a priori* calculation with no adjustable parameters.

IV. DISCUSSION

It is to be noted that the total shift between the exciton in the crystal and the gas phase value is predominantly determined by the interaction of the excited atom which interacts with the surrounding atoms more strongly than does an unexcited atom. In the case of Ne the repulsive forces are dominant, and hence the total shift is repulsive. The spin-orbit coupling is introduced by Cohen *et al.*¹¹ by considering only the Ne*($2p^5$) core (or p hole). So this formalism is indirectly similar to the intermediate coupling approximation. On introducing this interaction there results a large potential maximum around 5 a.u. in the 0_u^* (3P_1) from the crossing of $^1\Sigma_u^+$ and $^3\Pi_u$ curves. However, for this hump the repulsive shift for 3P states would have been much less than that of 1P_1 and not nearly equal to it. The attractive part being larger for 1P_1 than for 3P_1 , accounts for the reduction of spin-orbit splitting in the solid.

In Table II the shifts are quoted without any statement of error limits as Cohen *et al.*¹¹ do not

TABLE II. Collective contribution of the various interaction potentials for different states of pure solid neon. (Discrepancies of 0.001 eV between columns arise from truncation).

	1S_0	1P_1	$^1P_1-^1S_0$	3P_1	$^3P_1-^1S_0$	3P_2	$^3P_2-^1S_0$
Repulsive $V_{\text{Rep}}(R)$	0.015	1.399	1.384	1.381	1.366	1.031	1.016
Attractive $-C_6/R^6$	0.069	0.502	0.434	0.467	0.398	0.460	0.391
Attractive $-C_8/R^8$	<0.01	0.069	0.069	0.052	0.052	0.058	0.058
Resonance $-L_f^{\frac{1}{2}}$	0	0.097	0.097	0.087	0.087	0	0
$V_{\text{Rep}}(R) + C_6/R^6 + L_f^{\frac{1}{2}}$	0.054	0.800	0.853	0.827	0.882	0.570	0.625
$V_{\text{Rep}}(R) + C_6/R^6 + C_8/R^8 + L_f^{\frac{1}{2}}$	0.054	0.730	0.784	0.775	0.830	0.512	0.567

TABLE III. Comparison between experimental and calculated values E_f for the fundamental excitation of neon.

Atomic transition	Gas ^a	Oscillator strength ^a	Oscillator strength ^b	E_f solid ^c	E_f solid ^d	E_f experiment ^e	E_f experiment ^b
$^1P_1-^1S_0$	16.848	0.162	0.11	17.701	17.632	17.48	17.58
$^3P_0-^1S_0$	16.715		not allowed in the solid				
$^3P_1-^1S_0$	16.671	0.0118	0.11	17.553	17.500	17.48	17.48
$^3P_2-^1S_0$	16.619		not allowed in the solid				

^aIn the gas, from Ref. 19.

^bIn the solid, from the absorption reflection measurements of Pudewill *et al.* (Ref. 20).

^cPresent work: calculated shift with the repulsive, resonance and C_6/R^6 interactions plus gas phase energy.

^dPresent work: calculated shift with above interactions + C_8/R^8 plus gas phase energy.

^eFrom the absorption measurements of Boursey *et al.* (Ref. 7).

specify the accuracy of their results. Furthermore, the utilization of the Slater-Kirkwood¹⁴ relation is also subject to unknown errors. Thus, the agreement within 0.05 eV may be somewhat fortuitous, but this method seems promising for the rare-gas family, at least to deduce qualitative trends.

Now, regarding intensities, the 1_u (3P_2) becomes slightly allowed in the molecule at a distance of about 5.5 a.u., but, in the solid transitions to the $E_u + F_{2u}$ state to which the 3P_2 state is correlated as shown in Fig. 1, is strictly forbidden. For the molecule the 0_u^+ (3P_1) state becomes even more allowed as the $^1\Sigma_u^+$ component gains dominance over the $^3\Pi_u$ component when the interatomic distance decreases, but this change is relatively small. However, in the solid as each atom overlaps with 12 neighbors we conjecture that this would lead to a considerable enhancement of the 3P_1 state and this explains the nearly equal oscillator strength of the spin-orbit components in the solid. From the first derivative of the total potential of the excited and ground state one can deduce the shift of the exciton band with the lattice spacing. We find that it is about -0.07 eV per angstrom, so if the crystal expands the shift would be toward smaller energies. However, the zero-point displacement of the neon atoms in the solid would not produce any shift; on the other hand, it would lead to a broadening which can be estimated from the second derivative of the potential and the mean-square amplitude¹ of 0.29 Å. We find this to be about 0.08 eV, and this seems to be in qualitative agreement with the observed width of 0.05 eV of the two exciton bands.

We believe that the results obtained indicate a

new approach to the understanding of the exciton structure of solid rare gases and their relationship to the potential curves of the dimer and atomic spectrum. It would be possible to test this model on argon if first-principles calculations of the potential curves of the first excited states of Ar_2 are available, but we could probably even invert the procedure and obtain the isotropic part of the repulsive potential of the resonance states at the nearest-neighbor distance of the crystal, knowing the ground-state potential and the attractive part of the upper state. It is also clear why only Xe exhibits a shift to lower energies in the solid; this is certainly due to the very large polarizability of the excited states and the nearest-neighbor distance being so large that the attractive part dominates the picture. As this distance increases, we can predict that the shift will continue to increase toward lower energies. Only at very large distances would it approach gas phase values, but long before that the crystal would have melted. However, pressure-dependent studies would allow the determination of the repulsive potential at distances smaller than the potential minimum of the ground-state pair. Despite the lack of transparent windows in the first exciton region for lighter rare gases it may be open to study in the near future by multiphoton absorption.

ACKNOWLEDGMENTS

The authors wish to express their gratitude to Drs. K. Dressler, M. L. Klein, D. Oxtoby, and G. Zumofen for their attention to our work and their valuable comments.

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