

Biexcitons in solid neon

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We study the creation of biexcitons in neon films on a metal substrate by one-photon processes. We demonstrate that photon stimulated desorption of ions is a perfect tool for the investigation of these excitation processes which possess very low cross sections. We show that the principle of the equivalent core approximation which is well known from inner shell experiments can also be applied to the neon biexciton case. Comparing the equivalent core molecules Ne_2^{**} and Na_2 we find that neon biexcitons can be well described in a Frenkel picture.

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Introduction

Biexcitons or excitonic molecules are known since 1958 [1,2]. They arise from nonzero interaction energies of two excitons. They have been studied extensively in experiment as well as in theory (see, e.g., [3]). Recently they have attracted interest as objects for Bose–Einstein condensation, for nonlinear optical processes [4,5] and for quantum computing [5].

Most previous investigations focus on narrow gap insulators and on semiconductors [3,4], with a rapidly increasing interest in nanocrystals, microcavities, and quantum structures [6,7], and also in organic materials [8]. Biexciton binding energies in quantum structures can be very large [7]. The main signatures of biexcitons or excitonic molecules in these experiments are three different optical processes, namely the luminescence occurring when a biexciton decays into a single exciton, the inverse process where a biexciton is formed from a single exciton by photoabsorption, and the biexciton creation in a two-photon process with increased cross section, the so-called giant two-photon absorption [3].

More than a decade ago our group has shown that biexcitons exist in solid argon as well, and that these biexcitons can be excited in a one-step process either with electrons [9] or with photons [10]. Particularly the creation of two excitations on different centers in a solid by one photon is an interesting process. As has been shown by Dexter in the theoretical interpretation of experiments by Varsanyi and Dieke, the two excitations need to be coupled in order to enable nonzero

transition probability (see [11] and references therein). This is the case for excitons forming excitonic molecules, and in particular for the argon case, where the interaction energy is in the range of 10 to 20% of the one-exciton binding energy [10]. Despite the transition matrix element for one-photon biexciton excitation is nonzero due to this interaction, it is much smaller than matrix elements for one-electron excitations, or even for two-electron transitions where both electrons belong to the same atom [10,12]. In normal photoabsorption experiments, these biexcitonic one-photon absorption processes remain invisible on the large background of competitive transitions. In order to investigate them, we need a physical process which selectively projects them out.

Photon stimulated ion desorption (PSID) is such a projection tool. The solids of the light rare gases Ar and Ne show negative electron affinity [13]. The edges of their conduction bands lie above the vacuum level, i.e., the interaction between an additional electron and the closed shell Ar or Ne atoms forming the matrix is repulsive. This repulsive interaction is not only encountered by free electrons, but also by the extended wave functions of excitons. As a result, excitons are trapped in atomic centers by the creation of cavities around them. If this self-trapping occurs at the surface, the repulsive forces are unbalanced and the excited particles are ejected into the vacuum [13,14]. This process stimulates desorption of electronically excited atoms [13–15], dimers [16], and doubly excited dimers which correspond to the trapped form of biexcitons [9,10]. Singly excited atoms or dimers

de-excited by photon emission yield neutral products. For doubly excited dimers enough energy is available for autoionization. Depending on whether the autoionization process leads to bound or dissociative states of the final ionomer state, atomic or dimer ions are detected [9,10]. By evaluation of the dependence of the signal amplitude on the layer thickness, surface and bulk processes can be discriminated [9,10]. Because the competitive photoabsorption processes in the same energy range do not create ions, the biexcitonic processes can be separated in the experiment. We note that PSID is also helpful for the discrimination of multi-electron excitations with low cross sections in the inner shell excitation region [17].

In this paper we extend our previous study of argon to solid neon, the other rare gas solid with negative electron affinity. Our goal is threefold: Firstly, we want to demonstrate the potential of PSID for the discrimination of exotic excitations with low cross sections using another system as a typical example. Secondly, we show that biexcitons exist in solid neon as in solid argon (they probably exist also in the heavier rare gas solids where access via PSID by cavity ejection is not possible due to their positive electron affinities). Thirdly, we compare our biexciton results with theoretical data on Na_2 molecules and show that their electronic properties are very similar. From this we conclude that biexcitons in solid neon can be well described in a Frenkel, i.e., in a localized, molecular picture.

Experiment

All experiments were performed in a UHV chamber with base pressure better than $5 \cdot 10^{-9}$ Pa. For enhanced surface sensitivity, grazing incidence of the synchrotron light at 7 degrees with respect to the surface was used. We condensed the neon layers onto the (001) surface of a 7 K cold Ruthenium single crystal. Before dosing, we cleaned the substrate by sputtering with Ar^+ ions, repeated heating to 1450 K in 10^{-4} Pa of oxygen and final flashing to 1570 K. We checked the cleanliness of the substrate by x-ray photoelectron spectroscopy, and by thermal desorption spectroscopy of physisorbed xenon. The saturated Xe monolayer shows a desorption maximum associated with a 2D phase transition that is strongly suppressed by even very small amounts of impurities [18]. We note that a clean substrate is important for the perfect growth of Ne layers with minimum contamination. Reproducible amounts of neon (cleanliness better than 10^{-2} %) were dosed through a microcapillary doser onto the substrate. We calibrated the thickness of our films by comparing the relative areas of their thermal desorption peaks to those of well defined monolayers [19].

For TEY (total electron yield) excitation spectra, we used a simple PEY (partial electron yield) detector assembled from two grids and a large area electron multiplier. The grid assembly, which in the PEY mode served as a high pass for the emitted electrons was grounded for TEY. Desorbing ions were mass selected and recorded with a quadrupole mass spectrometer.

All measurement were done at TGM dipole beam-lines of BESSY, Berlin. The photon energy scale was recorded by taking gas phase photoabsorption spectra at elevated pressure (typically 10^{-5} Pa) in-situ, and by comparison with energy values from the literature.

Results and interpretation

Figure 1 shows Ne^+ and Ne_2^+ PSID spectra from a more than 100 layers thick neon film. Both signals show maxima at 33.5, 34.19, 35.6, 36.1, 36.85, and 37.8 eV. The maxima at 33.5 and 35.6 eV persist for films which are only 3 layers thick, for which the other structures vanish. We therefore assign them to surface excitations. The other features grow in for increasing thickness and saturate at about 100 layers. All these features can neither be assigned to resonant

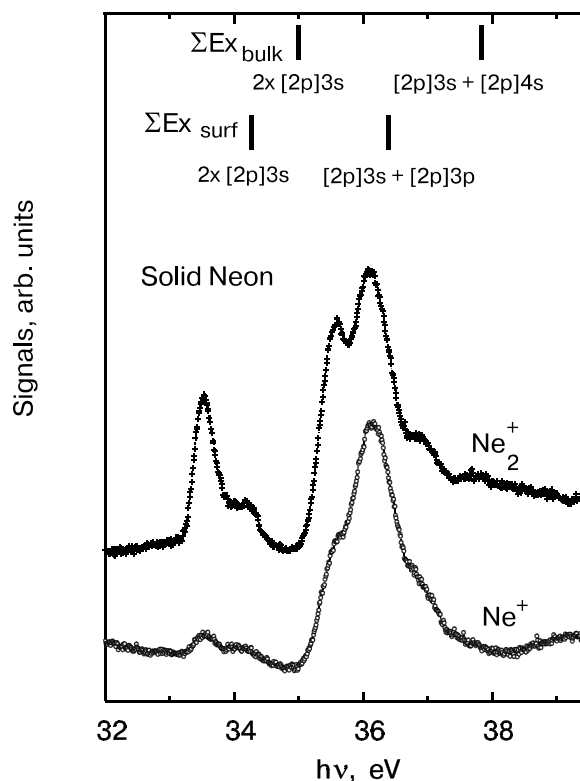


Fig. 1. TEY and photon stimulated desorption of Ne_2^+ and Ne^+ ions from a more than 100 layers thick Ne film. Sums of bulk ($[2p]3s$, $[2p]4s$) [20] and surface ($[2p]3s$, $[2p]3p$) [20–22] exciton excitation energies are indicated for comparison (multiplet structures have been averaged).

one-electron, nor to multi-electron states of a *single* neon atom. For condensed neon, no resonant one-electron states exist between the $[2p]$ ionization edge at 21.55 eV [20], and the lowest $[2s]np$ exciton around 47 eV [23,24]. The lowest two-electron excitation of a single neon atom occurs at 45.5 eV $\{\text{Ne}2p^4(^3P)3s(^2P)3p(^1P)\}$ at the surface [24] which is also well above the energy range of Fig. 1. The PSID peaks are, however, very close to the sums of two one-exciton excitation energies as indicated in Fig. 1, although not exactly at those positions. In particular the maximum at 33.5 eV is below the value which is obtained by doubling the energy of the lowest resonant excitation, i.e., the $[2p_z]3s$ surface state (we use the Frenkel notation here which we believe to be justified for the excitons with low principal quantum number of neon [25], and we have averaged the energetic positions of individual multiplet lines; we note that the normally dipole forbidden $[2p]3p$ excitation is exclusively seen at the surface with its reduced symmetry [21,22]). We therefore conclude that the maxima seen in PSID in this energy range must be due to excitations of excitonic molecules in a one-photon process because no other channels for a resonant process exist. The deviation of the peak positions from the sums of one-exciton excitation energies reflect the red-shift due to the binding of the excitonic molecules. These results resemble those obtained for argon to a large extent. As there, PSID is brought about by cavity ejection of localized biexcitons, and by subsequent autoionization and eventual (in the Ne^+ case) dissociation. Comparing the shapes of the Ne^+ and Ne_2^+ signals, we find that nondissociative autoionization is enhanced for the surface contributions. We believe that these excitations exist for the heavier rare gases as well, although PSID by cavity ejection is not possible, making their detection much more difficult.

In TEY, we found small features in this energy range which were not well reproducible. For thin layers and for reduced photon exposure, i.e., under conditions where charging and beam damage was minimized, they were below the detection limit. We therefore believe that these TEY structures were most likely due to secondary effects, i.e., accumulated lattice defects created by cavity formation and stimulated desorption. Lattice defects will affect the electron transport and charging, and this can cause modulations of the TEY as observed.

We have shown that biexcitons exist in solid neon and that PSID is a very powerful method for their detection. In the next step we try to analyze the main features of these excitations, namely their binding energy. We assume that we can describe them as localized excitons, i.e., in a Frenkel picture. The Frenkel,

i.e., the atomic picture, has been shown to be an appropriate description for the $n = 1$ ($= [2p]3s$) bulk exciton of solid neon [25]. We note, however, that for the excitons with higher quantum number and for the heavier rare gases the Mott–Wannier description is more appropriate. We further assume that we can apply the equivalent core approximation, which is a very powerful principle for the interpretation of inner shell excitation phenomena: A hole in an inner shell is small; its positive charge has nearly the same effect onto the outer orbitals which govern chemistry as an addition positive charge in the nucleus, i.e., the core excited atom behaves chemically like a $Z+1$ ground state atom. Holes in valence orbitals commonly are not small and usually not restricted to a single atom; so the equivalent core approximation can normally not be applied to them. Valence excited rare gases are however a special case because of their small ion radii. The interaction between two rare gas ions deviates from the Coulomb law only for small distances. This can be seen, e.g., from calculated potential curves for Ar_2^{2+} ([26]; unfortunately, similar data for Ne_2^{2+} do not seem to exist). The potential curves of the singlet states dissociating into two Ar^+ (2P) atoms are very close to $1/r$ for $r > 5$ bohr, which is much less than the next neighbor distance of solid Ar which is 7.1 bohr (see Fig. 1 of Ref. 26). For Ne, we expect similar relations. We therefore try to obtain the binding energies of the Ne biexcitons from its $Z+1$ analog which is a Na_2 molecule, see Fig. 2. We take Na–Na interaction energies from calculated Na_2 potential curves [27] for the next nearest distance of the Ne solid (5.97 bohr [28]), and add them to those sums of excitons energies which show the correct asymptotic behavior. Figure 3 shows the result. Particularly the two surface peaks at 33.5 and 35.6 eV are well reproduced by bonding Na_2 states aligned to sums of surface exciton energies. The

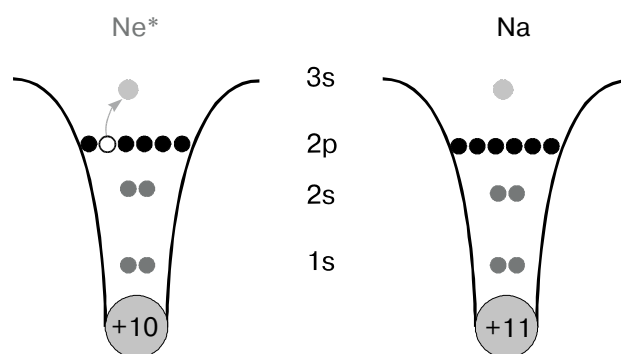


Fig. 2. Equivalent core picture: Assuming a small spatial extension of the $[2p]$ ionized Ne^+ ion core, a $[2p]3s$ excited neon atom corresponds to a sodium atom, and a $([2p]3s)_2$ excitonic molecule to a Na_2 molecule.

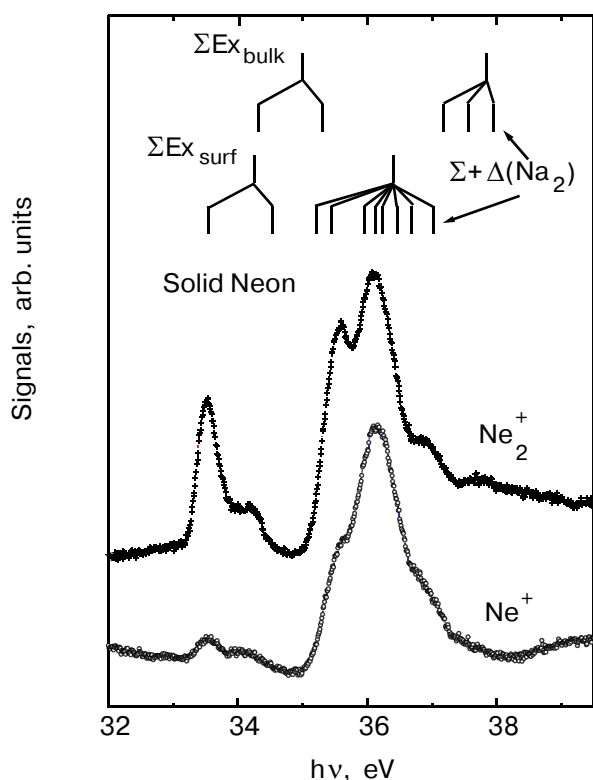


Fig. 3. Vertical bars: An estimate of biexciton energies obtained from the equivalent core picture (Fig. 2). The vertical bars denote energy positions obtained by adding Na–Na interaction energies from calculated Na_2 potential curves [27] to the sums of exciton energies. All values are for the next neighbor distance of solid neon. The positions in particular of the surface peaks of the experimental data are well reproduced.

peak at 34.16 eV which vanishes for thin layers is most probably the lowest bulk biexciton. The maximum at 36.1 eV can also be described by surface contributions, although combinations of bulk and surface states fit as well (not shown). The maximum at 37.8 eV could be due to bonding states dissociating into 3s and 4s bulk excitons; we admit, however, that the Frenkel picture may be not adequate for them because of their larger radii. Without straining the analogy too much, we find that the Na_2 analogy reproduces the lowest biexciton states of Ne surprisingly well.

In summary, we have shown that biexcitons exist for solid Ne as well, as found before for solid Ar. Their one-photon excitation cross sections are low, requiring sensitive experimental tools for their investigation. PSID is an ideal probe. Application of the $Z+1$ approximation reproduces the binding energies of the lowest bulk and surface biexcitons very well.

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