Resonant Coherent Excitation of Fast Hydrogen Atoms in Front of a LiF(001) Surface

C. Auth, A. Mertens, and H. Winter
Institut für Physik der Humboldt-Universität zu Berlin, Invalidenstrasse 110, D-10115 Berlin, Germany

A. G. Borisov
Laboratoire des Collisions Atomiques et Moléculaires, (Unité de Recherche associée au CNRS 281), Université Paris-Sud Bâtiment 351, F-91405 Orsay Cedex, France

F. J. García de Abajo
Departamento de CCIA, Facultad de Informática, UPV/EHU, Aptdo. 649, E-20080 San Sebastián, Spain
(Received 6 August 1997)

We have scattered protons and hydrogen atoms with energies of some keV from a LiF(001) surface under a grazing angle of incidence. From the intensity of Lyman-α radiation (transition from $n = 2$ to $n = 1$, $\lambda = 121.6$ nm) as a function of projectile energy for different azimuthal orientations of the crystal surface, we find clear evidence for a resonant coherent excitation of $n = 2$ states of hydrogen atoms in the oscillating electric field in front of the insulator surface. [S0031-9007(97)04713-3]

PACS numbers: 79.20.Rf, 34.50.Fa, 34.70.+e

When fast atoms or ions interact with a crystal under channeling conditions the target atoms induce oscillating electric fields in the projectile frame. Okorokov [1] predicted that for a corresponding setting of the projectile velocity and the crystal orientation these fields will stimulate a resonant coherent excitation (RCE) of electronic states in the projectiles. Early experiments with He^+ ions after the passage through thin crystal foils were not conclusive [2–4], since loosely bound electrons will not survive within the bulk of a metal. First evidence for RCE in a crystal was reported by Datz and co-workers [5–7] by observation of charge fractions of tightly bound hydrogenlike and heliumlike ions with MeV energies after the passage through thin crystals of Au and Ag. The enhanced ionization probabilities for electronically excited ions lead, under resonance conditions, to modified charge fractions which provide an unequivocal signature of RCE in a solid.

Kupfer *et al.* [8] proposed to make use of the electric fields that extend to the vacuum region in front of a solid and to excite electronic transitions in projectiles scattered in front of the surface ("surface channeling"). Attempts to observe RCE via optical transitions in He^+ ions failed [9]; however, recently Kimura *et al.* [10] found evidence for RCE by observing changes in the B^{4+}/B^{5+} charge ratios for MeV boron ions scattered under grazing incidence from a SnTe(100) surface. A structure in those ratios at a projectile energy of about 5.85 MeV is attributed to the $n = 1$ to $n = 2$ excitation of hydrogenlike boron ions (B^{4+}) via the second harmonic of the oscillating electric fields in front of the surface.

In this Letter we report on the first observation of RCE obtained for the scattering of fast atomic projectiles from the surface of an ionic crystal, here LiF(001). Our experiments demonstrate that making use of insulator instead of metal surfaces results in new attractive features which make ionic crystals well suited for detailed studies on resonant coherent excitation phenomena induced in the interaction of atomic projectiles with a solid target. We present results on the excitation of $n = 2$ in atomic hydrogen studied by the subsequent decay via Lyman-α radiation ($\lambda = 121.6$ nm). This work can be considered as the first successful resonant excitation of atomic levels with loosely bound electrons (binding energy some eV) in the interaction of fast atoms with solid matter.

Making use of an ionic crystal surface instead of metal or semiconductor crystal surfaces offers new features for studies on RCE of swift atoms:

The periodic potential in front of an ionic crystal results from the field of positive ions and negative ions at the alkali and halogen atom lattice sites, respectively. These charges are hardly screened by valence electrons which are localized at the negative halogen sites. For a point charge representation of the lattice, the potential for an electron in front of the surface ($z > 0$) is given by the analytical expression (atomic units),

$$V(\vec{r}) = \sum_{k,l>0} V_{kl}(z)\, \sin(kgx)\, \sin(lgy)\,, \qquad (1)$$

with the reciprocal lattice constant $g = 2\pi/d$ ($d = 7.6$ a.u. is the spacing between same lattice atoms along $\langle 100 \rangle$ strings), and

$$V_{kl}(z) = \frac{32\pi}{d^2}\, \frac{1}{g\sqrt{k^2 + l^2}}\, \frac{\exp(-g\sqrt{k^2 + l^2}\, z)}{1 + \exp(-0.5gd\sqrt{k^2 + l^2})}\,, \qquad (2)$$

where k, l denote the order of the harmonics and obey the selection rule $k + l =$ "even." The exponential dependence on z and the pronounced damping of amplitudes with k, l in Eq. (2) lead to a clear dominance of the fundamental frequencies ($k = l = 1$) in the potential $V(\vec{r})$

given by Eq. (1). This is in contrast to metals, where an efficient screening by conduction electrons gives rise to substantial contributions of higher order harmonics in the field [5,7].

The large band gap for insulators suppresses the loss of loosely bound electrons via resonant ionization to electronic states of the solid. Then atoms in excited atomic states with low binding energies (some eV) can survive from ionization in front of an insulator surface. For metals, those atoms will be efficiently ionized via resonant ionization to conduction band states (see, e.g., Ref. [11]) for distances where the surface electric fields may induce RCE.

These features of ionic crystal surfaces allow one to excite resonantly atomic states with low binding energies. Those states will not survive within a solid or at a metal surface, but will be stable in front of an insulator. RCE can then be studied via the emission of optical or near-optical radiation. Since this radiation can be analyzed with respect to its state of polarization, detailed information on the RCE process, not accessible so far in the "conventional" experiments performed with multicharged ions, could be obtained from the fluorescence light [8]. Furthermore, since the excitation energies amount to some eV, first order resonances can be observed at projectile energies in the keV domain, i.e., experiments on RCE can be performed with an ion source or a small ion accelerator.

The concept of our studies is discussed with the help of the energy diagram for the $n = 1$ and $n = 2$ levels of the hydrogen atoms in front of a LiF surface displayed in Fig. 1 (atomic levels are slightly shifted via image charge interactions). We used H^+ projectiles of some keV which are efficiently neutralized close to the surface via resonant electron transfer of electrons from the $F(2p)$ valence band to $n = 1$. At resonance, the electronic fields in front of the crystal may induce the excitation from $n = 1$ to $n = 2$, and if the distance to the atoms of the topmost layer of the crystal is large enough (e.g., compared to

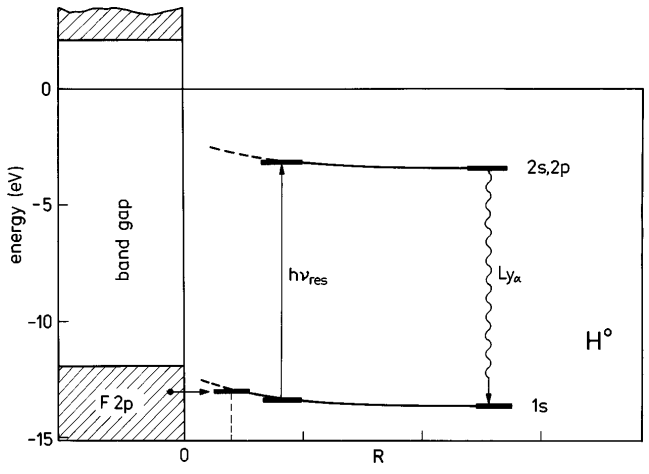

FIG. 1. Energy diagram illustrating the resonant coherent excitation of hydrogen $n = 2$ in front of a LiF surface.

orbital "diameters" of excited levels) the excited atoms will survive after the RCE and decay with a radiative lifetime $\tau \approx 1.6$ ns via the emission of Lyman-α photons of energy $\varepsilon = 10.2$ eV ($\lambda = 121.6$ nm).

In the experiments—performed under UHV conditions at a base pressure of 5×10^{-11} mbar—protons or neutral hydrogen atoms are scattered under a grazing angle of incidence Φ_{in} ranging from 0.3° to 2.5° from a LiF(001) surface. The target is kept at a temperature of about 300 °C in order to avoid a macroscopic charging up of the insulator [12] and is prepared by cycles of grazing sputtering with 25 keV Ar^+ ions and subsequent annealing at about 400 °C. The scattered projectiles are detected by means of a channeltron detector (entrance aperture 0.5 mm) positioned 380 mm behind the target. Well-defined angular distributions for scattered projectiles are observed with a FWHM less than 1° for energies of some keV. The energy loss of the projectiles is measured by means of an electrostatic energy analyzer.

The Lyman-α radiation is recorded with a channeltron viewing the region around the rear end of the target surface. A thin MgF_2 plate (cut-off wavelength $\lambda_{co} = 112.5$ nm) in front of the entrance of this channeltron results in a spectral response of our detector within $\lambda_{co} \leq \lambda \leq 150$ nm. So only the Lyman-α line ($\lambda = 121.6$ nm) of the emission from hydrogen atoms is detected.

The (projectile) energy resonance condition for planar channeling [13] is given by a similar expression as derived by Moak *et al.* [7]:

$$E_{res} = \frac{1}{8\pi^2} \frac{d^2 \varepsilon^2 M}{(l \cos\theta \pm k \sin\theta)^2}, \qquad (3)$$

where $\varepsilon = \frac{3}{8}$ a.u. is the atomic excitation energy and $M = 1836$ a.u. is the projectile mass (protons). The azimuthal angle θ is referred to a $\langle 100 \rangle$ axial channel in the (001) plane. As outlined above, we expect fundamental frequencies ($k = l = 1$) to dominate the RCE process completely. In this respect we note that we failed to observe higher order resonances in our experiments. Because of a frequency modulation resulting in sidebands, the resonance is split for an oblique incidence with respect to $\langle 100 \rangle$ ($\pm$ sign in Eq. (3), see discussion below and Refs. [7,8]). For our experiment we then derive $E_{res} = 5.14 \text{ keV}/(\cos\theta \pm \sin\theta)^2$, i.e., the projectile energies are in the keV domain. So far, evidence for RCE induced by solids has been observed only for energies of several MeV and even higher energies.

In Fig. 2 we show typical resonance structures observed with our setup for $\Phi_{in} = 0.75°$. We normalized the Lyman-α counts with respect to the intensity of scattered protons and scanned the projectile energy. Data for a scan from 2.5 to 8.5 keV and the projectile beam along $\langle 100 \rangle$ (solid circles) reveal a pronounced resonance structure with an enhancement of the signal by a factor of about 2 relative to a nonresonant background. For an azimuthal setting to $\theta = 4.5°$ (open circles) we find that the resonance signal is split into two peaks. This is

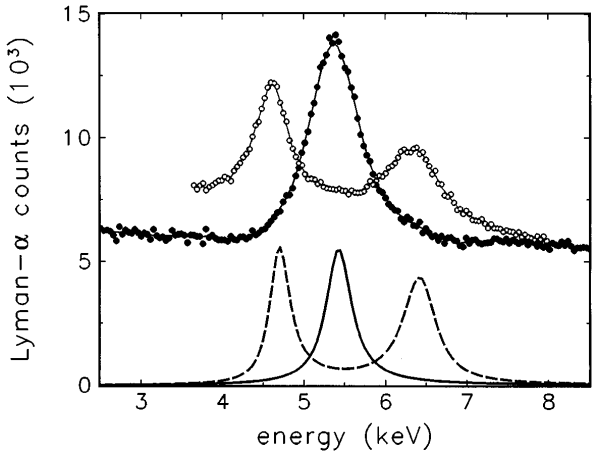

FIG. 2. Counts of Lyman-α signal as a function of projectile energy for the scattering of protons from a LiF(001) surface under $\Phi_{in} = 0.75°$. The data are normalized to the intensity of scattered projectiles. Full circles: $\theta = 0°$; open circles: $\theta = 4.5°$. The thin solid curves through the data are intended to guide the eyes; the thick solid and dashed curves represent results from our model calculations (see text).

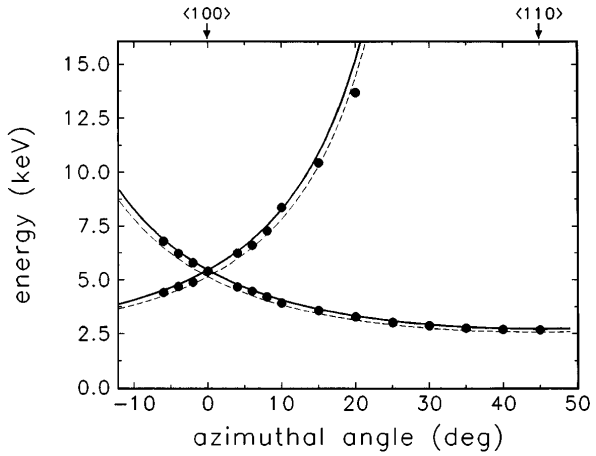

FIG. 3. Position of the resonance projectile energies as a function of azimuthal angle θ. The solid and dashed curves represent the resonance condition given in Eq. (3) *with* and *without* taking into account the total projectile energy loss, respectively.

the behavior expected for RCE under planar channeling conditions [7,8]. We could only speculate at present on the origin of the background, since our detector for radiation does not allow us to perform spectral scans. Contributions of vacuum ultraviolet (VUV) radiation emitted from the target are likely.

In Fig. 3 we have plotted the projectile energies at the peak positions as a function of the azimuthal angle θ (uncertainties correspond to the size of the symbols). The dashed curves in the figure represent the resonance condition given by Eq. (3). Since the projectiles lose energy during the scattering from the surface, the energy loss has to be taken into account and results in higher E_{res} as calculated. In studies on projectile energy loss we observe that the energy loss can be approximated by the linear dependence $\Delta E = 0.058E$. A correction of E_{res} by adding ΔE (solid curves) shows better agreement with our data. From the observed (split) resonances and, in particular, from the absolute agreement with the calculated resonance energies, we conclude clear evidence for the first observation of a resonant excitation of weakly bound atomic electrons in front of an insulator surface.

Aside from the demonstration of RCE via the radiative decay [14,15] in a new type of experiment and energy regimes for projectiles and photons not accessible so far, we can draw some conclusions on the excitation process itself.

In the analysis of the resonance energies, the projectile energy loss ΔE has to be taken into account (see Fig. 3). In a detailed study for $\theta = 0°$ ($\langle 100 \rangle$ direction), we find that the experimental resonance energy is increased from $E_{res} = 5.14$ keV derived from Eq. (3) under neglect of an energy loss by $\Delta E_{res} = (0.26 \pm 0.05)$ keV. Measurements on the projectile energy loss result in $\Delta E = (0.30 \pm 0.03)$ keV and an energy straggling $\delta E = (0.16 \pm 0.02)$ keV. Since ΔE_{res} is close to the projectile energy loss ΔE, we conclude that the RCE process will take place on the outgoing part of the trajectory, where the projectiles have undergone most of the energy loss. This interpretation is consistent with the simple concept that hydrogen atoms in $n = 2$ will be "quenched" close to the surface by binary collisions with surface atoms and periodic fields [16]. As a consequence, atoms excited close to the surface (distance of closest approach $z_0 \approx 2-3$ a.u.) will not contribute to the radiative decay of $n = 2$. Further support comes from the fact that the results obtained with incident protons or hydrogen atoms are comparable. In the case of the survival of excited states formed on the ingoing trajectory, one would expect to see effects on the initial charge state of the projectile.

Theoretical estimates on the resonance structure are obtained from solving the time-dependent Schrödinger equation in the projectile frame,

$$i\,\frac{\partial \Psi}{\partial t} = [H_0 + V(\vec{r}', t)]\Psi\,, \tag{4}$$

where $V(\vec{r}', t)$ is obtained from the potential given in Eq. (1) by transformation to the projectile frame. H_0 represents the Hamiltonian of the unperturbed hydrogen atom. The electron wave function Ψ is expanded in the five-state basis set of the $1s$, $2s$, $2p_x, 2p_y$, and $2p_z$ orbitals. We considered only the fundamental harmonics of the field ($k = l = 1$) and solved Eq. (4) on the outgoing path starting from $z_{ini} = 3.5$ a.u. for an initial occupation of the ground state.

The thick solid and dashed curves in Fig. 2 illustrate the results of our model calculations for the conditions met in the experiment (corrected by the total energy loss of the projectiles). It is evident that the main features observed in the experiments are reproduced. The results demonstrate that making use of ionic crystal

targets bears considerable potential for detailed studies on RCE processes; e.g., further insight into the excitation mechanisms could be obtained from the analysis of polarization phenomena in RCE [8]. In this respect, we find from our calculations a pronounced dependence of the populations of the different $2p$ states on θ.

The full half-widths of the calculated resonances are close to the broadening $\delta E_{\mathrm{res}} = 4\sqrt{2}\,E_{\mathrm{res}} \sin\Phi_{\mathrm{in}}$ caused by the finite interaction times with the oscillating fields. The experimental widths are somewhat larger. This we attribute to effects not included in our calculations, such as angle and energy straggling for scattered projectiles, reduced lifetimes of the excited states due to depopulation [17], and Stark splittings. Experimentally, we observe an increase of δE_{res} with angle Φ_{in} as expected for a broadening due to reduced interaction times; however, a detailed discussion is beyond the scope of this paper.

In conclusion, we presented unequivocal evidence for the resonant coherent excitation of $n = 2$ states of fast hydrogen atoms in grazing scattering from the surface of an ionic crystal, here LiF(001). Our data represent first measurements of RCE of electrons loosely bound in an atom probed via the emission of (near) optical radiation. The suppression of resonant ionization due to the band gap, as well as the clear dominance of fundamental resonances, makes ionic crystals ideal targets for detailed studies on RCE processes induced in fast projectiles interacting with solids. Finally, we point out that our results lead to progress in the understanding of the charge transfer of atoms in front of insulator surfaces. The data support the interpretation of electron loss via the kinematically assisted excitation of electrons bound at the projectiles to conduction band and vacuum states. This plays, e.g., an important role in the formation of negative ions during grazing scattering of fast atoms from alkali halide surfaces [18–20].

The assistance of A. Göhnermeier, A. Kirste, M. J. Steiner, P. Wolf, and R. A. Noack in the preparation and running of the experiments is gratefully acknowledged. This work is supported by the Deutsche Forschungsgemeinschaft under Contract No. Wi 1336.

[1] V. V. Okorokov, JETP Lett. **2**, 111 (1965).
[2] M. J. Gaillard, J. C. Poizat, J. Remillieux, and M. L. Gaillard, Phys. Lett. **45A**, 306 (1973).
[3] H. G. Berry, D. S. Gemmell, R. E. Holland, J. C. Poizat, J. Remillieux, and J. N. Worthington, Phys. Lett. **49A**, 123 (1974).
[4] M. Mannami, H. Kudo, M. Matsushita, and K. Ishii, Phys. Lett. **64A**, 136 (1977).
[5] S. Datz, C. D. Moak, O. H. Crawford, H. F. Krause, P. F. Dittner, J. Gomez del Campo, J. A. Biggerstaff, P. D. Miller, P. Hvelplund, and H. Knudsen, Phys. Rev. Lett. **40**, 843 (1978).
[6] C. D. Moak, S. Datz, O. H. Crawford, H. F. Krause, P. F. Dittner, J. Gomez del Campo, J. A. Biggerstaff, P. D. Miller, P. Hvelplund, and H. Knudsen, Phys. Rev. A **19**, 977 (1979).
[7] C. D. Moack, J. A. Biggerstaff, H. Crawford, P. F. Dittner, S. Datz, J. Gomez del Campo, P. Hvelplund, H. Knudsen, H. F. Krause, P. D. Miller, and S. H. Overbury, Nucl. Instrum. Methods **194**, 327 (1982).
[8] E. Kupfer, H. Gabriel, and J. Burgdörfer, Z. Phys. A **300**, 35 (1981).
[9] K. Kimura, M. Hasegawa, Y. Fujii, Y. Susuki, and H. Mannami, in *Ion Beam Interactions with Solids*, edited by F. Fujimoto (North-Holland, Amsterdam, 1988) p. 257.
[10] K. Kimura, H. Ida, M. Fritz, and H. Mannami, Phys. Rev. Lett. **76**, 3850 (1996).
[11] P. Nordlander and J. C. Tully, Phys. Rev. Lett. **61**, 990 (1988); Phys. Rev. B **42**, 5564 (1990).
[12] P. Varga and U. Diebold, in *Low Energy Ion-Surface Interactions*, edited by J. W. Rabalais (Wiley, New York, 1994), p. 355.
[13] D. S. Gemmell, Rev. Mod. Phys. **46**, 129 (1974).
[14] Y. Iwata, Y. Hirao, T. Hasegawa, M. Sekiguchi, A. Mizobuchi, T. Hattori, and K. Kimura, Nucl. Instrum. Methods Phys. Res., Sect. B **33**, 354 (1988).
[15] S. Datz, P. F. Dittner, H. F. Krause, C. R. Vane, O. H. Crawford, J. S. Forster, G. S. Ball, W. G. Davies, and J. S. Geiger, Nucl. Instrum. Methods Phys. Res., Sect. B **100**, 272 (1995).
[16] F. G. Garcia de Abajo and P. M. Echenique, Phys. Rev. Lett. **76**, 1856 (1996); Nucl. Instrum. Methods Phys. Res., Sect. B **115**, 229 (1996).
[17] A. Salin, A. Arnau, and P. M. Echenique, (to be published).
[18] C. Auth, A. G. Borisov, and H. Winter, Phys. Rev. Lett. **75**, 2292 (1995).
[19] H. Winter, C. Auth, and A. G. Borisov, Nucl. Instrum. Methods Phys. Res., Sect. B **115**, 133 (1996).
[20] F. W. Meyer, Q. Yan, P. Zeijlmans van Emmichoven, I. G. Hughes, and G. Spierings, Nucl. Instrum. Methods Phys. Res., Sect. B **125**, 138 (1997).