JSPS-NSF and RIKEN

Joint Workshop on Resonances in Physics, Chemistry and Biology
(US-JAPAN Workshop)

December 18-20, 2002, Hayama, Japan

Book of Abstract

Resonance Tuning and Detuning Phenomena
in
Muon Catalyzed Fusion (μCF)

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Negative muon (μ^-), which has 207 times heavier mass than that of electron, can catalyze nuclear fusion reactions among hydrogen isotopes (p, d, t) by forming a small muon molecular ion e.g. $(dd\mu)^+$, $(dt\mu)^+$. In some cases, in particular for the d-t μCF, the catalyzed fusion reaction can be repeated upto more than 100 times within muon life time (2.2 μs), providing us an expectation of the use for atomic energy related applications. It is well-known that the formation of muon molecular ion like $(dd\mu)$ and $(dt\mu)$ proceeds quite rapidly to the shallowest molecular state by a resonant reaction between $(d\mu)+D_2$ and $(t\mu)+D_2$, respectively. After a series of related experiments conducted rather recently, the following surprising phenomena was discovered; at low-temperature, e.g. in solid-phase, resonance tuning occurs for $(t\mu)+D_2$, while resonance detuning occurs for $(d\mu)+D_2$.

Details of experimental results, possible explanations and implications towards future developments will be presented.

Correlation in Antiproton Capture by Atoms and Molecules

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Antiprotonic ($\bar{p}$) atoms are formed in low-energy collisions between antiprotons and normal atoms or molecules. There is renewed interest in this subject due to upcoming experiments (ASACUSA Collaboration), which, for the first time, can directly measure the energy-dependent cross sections. This can be done for capture by the hydrogen molecule *and* atom, as well as for capture by the noble-gas atoms. The only existing accurate capture cross sections calculated purely quantum mechanically are for the hydrogen atom below 10 eV. They are in good agreement with a number of other more approximate calculations. Comparison between theory and experiment for this simplest system will be important in confirming that most captures occur after the $\bar{p}$ has been slowed to a kinetic energy less than or comparable to the target ionization potential. This problem can be interpreted as a case of a resonant state embedded in an electronic continuum, *a la* the Fermi Golden Rule.

However, there are other fundamental effects due to correlation and the additional degrees of freedom in multielectron atoms and molecules. The fermion molecular dynamics (FMD) method has enabled us to go beyond the atomic hydrogen target and study electron-correlation effects with noble-gas targets and molecular effects with isotopic molecular hydrogen targets. FMD is a quasiclassical method for treating quantum-mechanical systems using classical equations of motion with momentum-dependent model potentials added to the usual Hamiltonian to simulate quantum-mechanical effects. These model potentials constrain the motion to satisfy the Heisenberg uncertainty and the Pauli exclusion principles. In this method, correlation and rearrangement are simple.

The differences between capture by H_2 and the H atom are found to be dramatic. The effects due to the two-center structure, rotational motions, and vibrational motions are distinguished. Of particular importance, the vibrational degree of freedom enables the molecule to capture antiprotons

having lab energies above 100 eV, whereas atomic capture cuts off sharply above the ionization threshold of 27 eV (in the lab system). The largest molecular cross sections are obtained when the negative projectile mass best matches a nuclear mass in the molecular target. The vibrational degree of freedom is found to be most important in distinguishing capture by H_2, HD, and D_2, but the effects of rotations, two-center electronic charge distribution, and nonadiabaticity are also significant.

Antiproton captures by helium, neon, argon, krypton, and xenon atoms have also been treated using the FMD method. The residual electrons are generally left in a shake-up state. When capture is accompanied by multiple ionization, the second and later electrons are seen to escape with increasing kinetic energies, a process which is not well described as quasiadiabatic. In agreement with experiments on muonic and pionic atoms (none exist for antiprotons yet), the capture probabilities are found to increase with increasing numbers of electrons. This is opposite the trend predicted by a recent theoretical treatment using a quantum-mechanical *one-electron* method and provides evidence of the importance of electron-electron correlation.

The important electronic continua and molecular dissociation are easily, and perhaps accurately, treated quasiclassically. However, the quasiclassical method does not quantize the final states, so the effects of shake-up electronic states, excited ro-vibrational levels, and associated resonances may not be treated adequately. In addition to presenting some surprising results, I hope to initiate a dialog on what features will be important for a completely quantum-mechanical description and what possibilities exist for such capabilities.

Resonances in Dissociative Recombination

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Dissociative recombination (DR) of molecular ions:

$$AB^+ + e^- \rightarrow AB^\dagger \rightarrow A + B^*$$

transforms the kinetic energy of the incident electron into excitation of the core electrons. DR occurs when the dominant configuration of $AB^\dagger$ corresponds to a repulsive state and the chemical bond is broken. This is an important process in low temperature plasmas, such as interstellar clouds, planetary atmospheres and in plasma processing such as chemical vapor deposition[1]. With some notable exceptions[2], the process is dominated by resonances.

These resonances include both the repulsive $AB^\dagger$ states, but also bound states lying in the same energy range which lead to structure in the DR across section as a function of initial electron energy. These structures are the signature of the "indirect" recombination process. In general, they can be assigned to excited rovibrational levels of bound Rydberg states with a ground-state ion core, which couple to the initial ground-state electronic continuum by non-adiabatic interactions only.

In addition, there exists another class of resonances. These are members of a Rydberg series converging to excited states of the ion, generally referred to as "core-excited" states. These states are bound with respect to dissociation, if the ion to which the series converges is bound. They are coupled both to the electronic initial continuum and to the dissociative final channel and tend to produce broader and more prominent structures in the DR cross section[3].

We will illustrate each of these resonances for the case of dissociative recombination of the water ion. DR of the water ion is the source of OH radicals in the H I zone in dense molecular clouds[4]. Both the absolute cross section and the branching ratios in the final neutral fragment channels have been measured[5].

The ground state of water is:

$^2A_1 \qquad (1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$
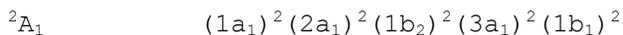
The water ion has three low-lying excited states resulting from removing one electron from the three lowest lying orbitals.

$^2B_1$ $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)$

$^2A_1$ $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)(1b_1)^2$

$^2B_2$ $(1a_1)^2(2a_1)^2(1b_2)(3a_1)^2(1b_1)^2$

Each of these low-lying states has a Rydberg series of neutral water curves associated with it. For the case of the two higher states, some of the Rydbergs lie above the ground state of the ion, forming core-excited states. There also exist dissociative neutral autoionizing states that cross the ground state of ion that can lead to DR.

Electron-scattering calculations from the molecular ion using the complex Kohn variational method have been carried out in C_{2v} geometry. The eigenphase sums were fit to a Breit-Wigner form and the resonance energies and autoionization widths were obtained. The variation of the states as a function of the symmetric stretch and bend will be presented and the implications for dissociative recombination of the water ion and the final states resulting from this collision process discussed.

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Experimental Study of Momentum-transfer Cross Section and $^1Z_{\text{eff}}$ for Slow Positronium-Gas Collisions

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It is possible to extract useful quantitative information on Positronium (Ps) interactions at lower energies using the angular correlation of annihilation radiation (ACAR) method combined with the use of silica aerogel. The material has also been employed in the studies of ortho-positronium (o-Ps) through lifetime technique. The silica aerogel is a three-dimensional network composed of silica grains. Since the free space between the grains is connected to the outer space, the gas atoms or molecules to be investigated can diffuse immediately into the inner space. When positrons from a radioactive source are injected into this material, about half of the positrons form Ps atoms in the grains or on the surface of the grains. The Ps atoms are emitted into the free space due to the negative work function for SiO_2 with an emission energy of about 0.8 eV. The Ps atoms then interact with the atoms/molecules in the space and with the grain surfaces.

The momentum-transfer cross sections for positronium (Ps)-gas scattering in the low energy region have been obtained by using the one-dimensional angular correlation of annihilation radiation (1D-ACAR) method; the momentum distributions of Ps in the gases are measured as functions of mean lifetime of Ps varied by applying a magnetic field. The average energy obtained for o-Ps with mean lifetimes of 3 to 90ns is analyzed assuming that the Ps is thermalized by elastic scattering with gas atoms/molecules. In the low energy region, Ps is actually thermalized mainly through elastic scattering with diatomic and polyatomic molecules as well as inert gases.

The parameter characterizing the pickoff annihilation rate of Ps, $^1Z_{\text{eff}}$, is also studied using silica aerogel. Iwata et al. has reported a large increase in the parameter Z_{eff} characterizing positron annihilation in gases, suggesting formation of resonances or bound states in large molecules. It is thus worth performing a systematic study for the Ps annihilation counterpart. Our study has revealed that $^1Z_{\text{eff}}$ increases linearly with the molecular polarizability with a somewhat exceptional behavior of Xe. A good correlation is also found with the geometrical cross section of the molecule. This indicates that the Ps pickoff annihilation takes place without forming a resonance or a bound state.

Discrimination of spin conversion (ortho-para conversion) and pickoff conversion of Ps in sxygen will also be reported.

Energy-resolved Measurements of Positron Annihilation on Large Molecules[+]

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The mystery of very large annihilation rates for positrons interacting with large molecules (e.g., containing several atoms) has remained unsolved for decades [1, 2]. In many cases, annihilation rates are orders of magnitude larger than expected from simple, uncorrelated collisions. Also, annihilation rates are often found to increase exponentially with molecular size. This phenomenon is important, not only in atomic and molecular physics, but it is also potentially relevant to annihilation in astrophysical settings and in materials such as organic solids. Theoretical models of these positron-molecule interactions have been proposed which incorporate Feshbach resonances associated with the vibrational modes of the target molecule [4], but prior to the studies described here, evidence of these resonances had remained elusive. Measurements of the normalized annihilation rate, Z_{eff}, as a function of incident positron energy will be presented for a variety of molecules, made using a cold positron beam (~25 meV FWHM) [3]. Incident positron energies ranged from 50 meV to the Ps threshold. The resulting energy-resolved data show large enhancements near the energies of the molecular vibrational modes. To our knowledge, these experiments provide the clearest example of a resonance phenomenon in either positron-atom or positron molecule interactions. Several features in the data lead to the conclusion that these resonances are intimately connected with the large annihilation rates observed previously using thermal distributions of positrons at 300 K. Further, the observed energies of the resonance peaks are downshifted from the vibrational mode energy. This downshift is interpreted as a measure of the positron-molecule binding energy, ranging from 40 meV in butane (C_4H_{10}) to 210 meV in dodecane ($C_{12}H_{26}$). This experiment provides the first experimental evidence that positrons can bind to neutral atoms and molecules. Recent experimental data will also be discussed, focusing on changes in the binding energy with varying molecular size and shape in alkanes, and on Z_{eff} measurements of smaller and simpler molecules than in previous work (e.g., triatomics and fluorinated methanes). The data confirm key features of a recent treatment of the vibrational Feshbach resonance model [4]. The talk will conclude with a brief discussion of a number of important questions that remain to be addressed regarding positron annihilation on molecules.

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Resonances in $\mathrm{e}^+ + \mathbf{He}^+$ System

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A three body system involving electron, positron and He^{2+} is considered. For the negative total energies, two possible arrangements in the asymptotic region are $\mathrm{He}^{2+} + \mathrm{Ps}$ and of $\mathrm{e}^+ + \mathrm{He}^+$. There exists attractive long range potentials in the former arrangements, namely, the polarization potential in the ground state Ps channel and the dipole potentials in the excited state Ps channels. Infinite series of resonances occur below the excited states Ps thresholds due to the long range dipole potential. While, the interaction at a large distance is dominated by a repulsive coulomb potential in the latter arrangement, and the channels which dissociate into $\mathrm{e}^+ + \mathrm{He}^+$ do not have many resonances.

Resonance calculations have been performed using the stabilization method[1], the complex rotation method,[2], and the hyperspherical close coupling (HSCC) method, [3] however, there are disagreements in the existence of resonances among these calculations.

We reexamine the S-wave resonances using the HSCC method, and show the results in the meeting.

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Resonance Phenomena in Electron Capture Processes by Multiply Charged Ions

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At low collision energies, interesting phenomena such as shape resonance and orbiting appear in electron capture processes [1-3]. Shape resonance causes peaks in cross sections at particular collision energies because quasi-molecules are formed during collisions. Furthermore, orbiting causes a monotonic increase in cross sections with decreasing velocity. Mechanism of orbiting is usually explained by classical scattering trajectories such as projectile ions rotating around target atoms [4].

Shimakura and Kimura (1991) have reported that shape resonance and orbiting occur in electron capture by N^{5+} ions from H atoms [2]. However, the dynamical mechanism of shape resonance was not evident because a time-independent close-coupling method was used in their calculation. In this work, we show the examples of the shape resonance for some systems and then provide a dynamical picture of shape resonance for the case of (N^{5+} + H) system by using a multi-channel wave packet method that can solve the time-dependent close-coupling equations in order to elucidate the mechanisms of shape resonance. The method based on the split-operator technique is efficiently implemented with the aid of fast Fourier transform [5].

Figure 1 shows the cross sections of the N^{5+} + H collision calculated by using a time-independent close-coupling method. In this calculation, only three Σ states are considered, $i.e.$, 1Σ, 2Σ, and 3Σ states corresponding to the $N^{4+}(4s)$ + H^+, $N^{4+}(4p)$ + H^+, and N^{5+} + H (1s) states at the separated atom limit, respectively. The solid and broken lines in figure 1 represent the partial cross sections of the $N^{4+}(4s)$ + H^+ and $N^{4+}(4p)$ + H^+ states, respectively. Several peaks appear below $E = 0.02$ eV/amu. Squared scattering matrices around collision energies at which peaks appear show that each peak is dominated by the partial wave with a particular angular momentum K. This indicates that in the effective potentials with such angular momenta quasi-bound states are formed and the effective potential produces a well with a centrifugal barrier. Thus, shape resonance occurs when the collision energy coincides with that of the rovibrational state of the quasi-molecule. The peaks can be assigned to vibrational v and rotational K states. The rovaibrational states (v, K) used for the assignment in Fig.1 are quasi-bound states of the adiabatic 3Σ effective potential and the states (v, K)* are those of the diabatic potential smoothly connecting the adiabatic 2Σ and 3Σ effective
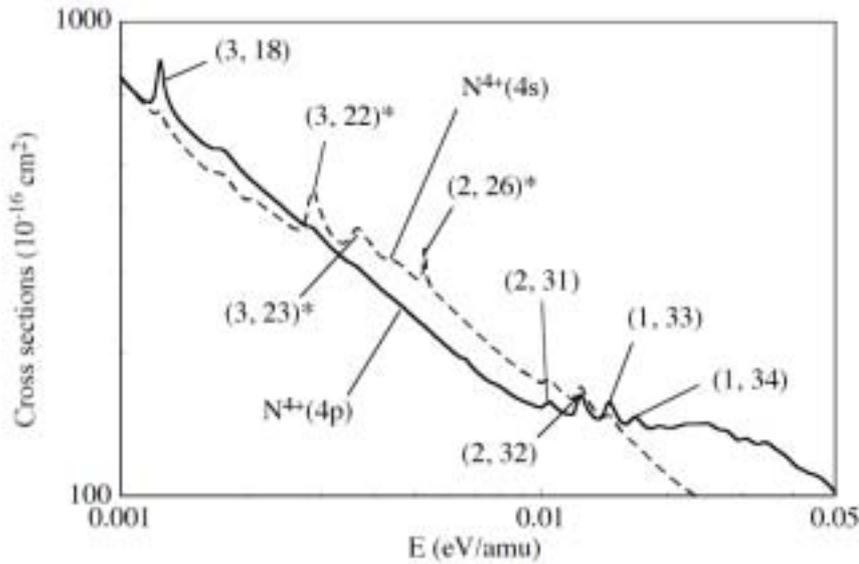
Fig. 1. Electron-capture cross-sections in the (N^{5+} + H) collision system. The partial cross sections of the N^{4+}(4s) + H^+ and N^{4+}(4p) + H^+ states are denoted by solid and broken lines, respectively. The peaks are assigned to resonance rovibrational states (*v*, *K*) and (*v*, *K*)*. The definitions of these states are given in the text.

potentials. These rovibrational states and energies were obtained by using the Rydberg-Klein-Rees method [6-9].

To demonstrate the time-dependent picture of shape resonance for the resonance state, we calculate the wave packet dynamics. In the calculation of the dynamics, all the three potentials and non-adiabatic couplings between them are taken into account. The calculated results show many useful concepts about the shape resonance. After some times elapse, part of the wave packet is trapped into the quasi-bound potential of the 3Σ state; the other part is scattered by the centrifugal barrier. As obvious from the increase in the 2Σ component, the wave packet trapped into the quasi-bound potential transfers to the N^{4+}(4p) + H^+ channel rather than returns to the initial channel by tunneling again. We also examine a case where the collision energy is off from that of the rovibrational state. In this case, the wave packet does not tunnel through the centrifugal barrier when the collision energy does not match with the resonance energy.

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Inseparable positron annihilation and positronium formation in positron-hydrogen collisions

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A unified treatment of positron annihilation and positronium (Ps) formation in collisions of positrons with hydrogen atom is presented. The effects of the positron annihilation are directly included in the Hamiltonian as an absorption potential, and hence the finite lifetimes of Ps in ns states are automatically taken into account. The Schrödinger equation is solved using the close-coupling method in terms of hyperspherical coordinates. This theory elucidates that, near the Ps(1s) threshold E_{th}, the annihilation and Ps formation in the conventional sense are inseparable, and that Ps formation constitutes just a part of annihilation as an indirect process. Thus the annihilation cross section, which would diverge close to E_{th} if Ps(1s) had an infinite lifetime, is found to connect smoothly across E_{th} to the cross section for Ps formation, which is meaningful only at energies well above E_{th}. A preliminary report of this work has been published elsewhere [1].

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Electron-impact vibrational excitation of CO_2
– Recommended data on the cross section –

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An electron collision with CO_2 plays a fundamental role in many application fields (e.g., atmospheric physics, gaseous discharges, plasma processing etc.) Because of its long history, there are a large number of papers reporting cross section data for the process. It would be valuable, therefore, to compile those data to produce a set of cross sections recommended for use. Such an attempt has been made recently.[1)] Here, as an example, the result for the vibrational excitation is presented.

Very recently Kitajima et al. made a crossed-beam experiment to measure the differential cross section for the vibrational excitation of CO_2 at the angles of 10-130 deg and the energies of 1.5-30 eV.[2)] From the experimental data, supplemented with the recent theoretical calculation,[3)] integral cross sections have been derived to recommend.   For the region of the energies below 1.5 eV, the result of a recent swarm-type measurement by Nakamura[4)] could be used. While the swarm results for (010) and (001) excitations are consistent with the recommended values in the higher-energy region, those for (100) are not smoothly connected with the higher-energy values. In 1985, Kochem et al. reported their beam-type measurement of DCS at the energies below about 1 eV.[5)] They succeeded in obtaining integral cross sections only for (100) excitation.   Their cross section for (100) is consistent well with the values recommended above.   The tentative conclusion for the recommended data below 1.5 eV is: cross sections from a beam-type measurement of Kochem et al. for (100) and the swarm data of Nakamura for (010) and (001).   To confirm this conclusion, we need further theoretical and/or experimental studies.

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Nuclear-excited Feshbach resonance in Penning ionization reactions

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Combination of oriented molecular beam method with time of flight technique makes us possible to determine orientation-angle and collision-energy specified Penning ionization cross sections for CH_3X (X= Cl, Br, I) reactions. Remarkable oscillation structures in collision-energy dependence of the ionization cross section are observed only if we control molecular orientation. This resonance-type structure can be interpreted as a new type of nuclear-excited Feshbach resonance, where neutral dissociation process competes with the ionization through formation of vibrationally excited CH_3X Rydberg state.

We prepare an oriented halo-methane CH_3X (X=Cl,Br,I) molecular beam by a 70-cm electrostatic hexapole state-selector and the oriented molecular beam crosses Ar* metastable argon beam which is generated by a short-pulse grow discharge. Orientational distribution of the CH_3X oriented beam can be determined from experimental focusing curve. Under three types of molecular orientations experimentally prepared prior to reaction, namely the CH_3-end, the X-end, and random orientations, reaction takes place and produces CH_3X^+. TOF profiles of the product ions were measured. The orientation-angle and collision-energy resolved cross section, called 3D-plot, is then obtained. In the 3D-plot for Ar*+CH_3Br reaction, remarkable oscillation structures can be seen along collision energy axis. The amplitude oscillates with narrow energy widths, so that we will see that this resonance-type structure is caused by branching competition via indirect dissociative recombination during Penning ionization, which leads to neutral dissociation channel. An *ab initio* calculation suggests that there are many CH_3Br Rydberg states near the ionization threshold, and that they are excited in vibration. The energy positions of the oscillation in the experimental cross section are found to be parallel to the energy levels of the Rydberg states calculated. Within the experimental energy region, only three vibrationally excited states, $2v_1$, $2v_4$ and $2v_1+v_3$ -vibrational modes of $E_{3/2}$ can be energetically accessible. Therefore, the present result suggests that such new resonance-type structure is closely relevant to vibrationally excited Rydberg states that are coupled with dissociative dissociation exit channels. Similar good correlation between the experimental results and the calculated energies is also recognized for other Penning ionization reactions we have studied so far.

Linear and Non-Linear Optical Responses of Exciton Fano Resonance in Semiconductor Heterostructure

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Quantum interference between continua and a discrete level embedded in the former gives rise to a pronounced asymmetric spectral profile having a peak-and-dip structure, known as Fano resonance (FR). It is well known that this phenomenon plays significant roles in nuclear, atomic and molecular physics for the studies of energy-structures of highly-excited states and the related relaxation dynamics due to interparticle correlation. Recently, the FR of exciton states has been intensively investigated in quantum wells (QW's), quantum wires, and superlattices with and without external electric and/or magnetic fields. These FR states arise from interactions of subbands ascribable to quantum confinement of these semiconductor heterostructures. Here a subband is also termed a channel. The interchannel interactions are classified into Coulomb coupling and valence-band mixing, where in-plane angular momenta of concerned channels remain unaltered in the former and the change of them is accompanied by the latter. Usually, the former coupling is considered dominant to the latter one.

The present talk is mainly focused on spectral modulation and further coherent control of FR of the low-dimensional exciton states with respect to material parameters and irradiated-laser parameters. The coherent control of quantum states is one of the current hot topics, extending over wide interdisciplinary fields of atom, molecule and semiconductor physics, non-linear optics, quantum electronics, laser science, and so on [1]. Aside from academic interests in the novelty, especially, these studies allow to open new possibilities of optoelectronic device engineering and laser technology.

First, linear absorption spectra of QW-exciton FR states are presented, where the FR profiles vary conspicuously with increasing well thickness d. This is due to the valence-band mixing effect that enlarges overlap with adjacent FR states with d larger [2]. In Fig. 1, FR spectra of the $B : [2,2]^h$-exciton are given for several GaAs/Al$_{0.3}$Ga$_{0.7}$As-QW's of $d = 10-50$ nm. A heavy-hole exciton state, above all, $B1$, usually manifests itself as dominant resonance. These spectra are calculated by solving multichannel scattering problems pertinent to the present FR system by use of the R-matrix propagation technique [3]. This method provides calculations with high accuracy comparable to the recent high-resolution measurements of various exciton FR states [4]. The similar overlap resonance is also observed in excitons in biased superlattices when an applied dc-electric field F_0 normal to the layer plane is changed. For large (small) F_0, carriers are spatially localized (delocalized) in the crystal growth direction. This type of superlattices is termed the Wannier-Stark ladder (WSL).

Second, four-wave mixing (FWM) spectra of the WSL-exciton FR are considered in both temporal and frequency domains [5]. FWM with two (pump and probe) pulse-lasers arranged is one of the most powerful technique for examining non-linear optical response and transient relaxation dynamics. Strength of coupling between the irradiated pump laser field and exciton states can be optionally tuned so as to be comparable to or larger than that of the Coulomb coupling leading to the FR. Furthermore, many-body effects of exchange interactions between excitons become significant here, since interband transitions induced by this relatively strong pump laser generate a great number of electron-hole pairs. The many-body effects, giving rise to increase of self-energies of excitons and vertex-corrections associated with the generalized Rabi frequency, are characteristic of laser-material interactions in semiconductor systems, differing a lot from those in atom and molecule systems [6]. It is shown that these two couplings, namely, pump laser-exciton and exciton-exciton interactions, play notable roles for strong modulation and coherent control of FR states transiently formed for the duration of irradiation of the two fs-laser

pulses. This behavior is reflected in the time-resolved FWM spectra and the relevant power spectra. Figure 2 shows that the many-body effect contributes to prominent modulation of the power spectra in 3.4nm-GaAs/1.7nm-$Al_{0.3}Ga_{0.7}$As-superlattices with $F_0 = 25$ kV/m. The numerical results are provided by solving the semiconductor Bloch equations with using exciton FR states as an expansion basis set [3].
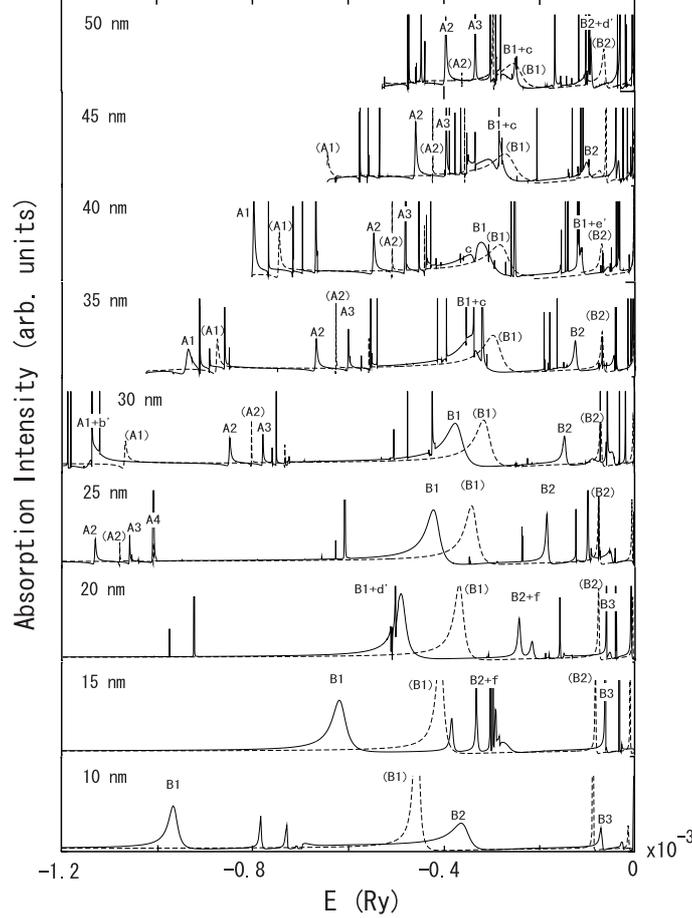
Figure 1: Absorption spectra of FR states pertaining to the channel B in GaAs/$Al_{0.3}Ga_{0.7}$As-QW's of 10-50 nm versus an energy E reckoned from the subband energy of this channel. Here, each subband for a heavy-hole (HH) (a light-hole (LH)) exciton is designated as $[n_e, n_h]^{h(l)}$, with n_e and n_h electron and hole quantum numbers of respective QW's. Channels of optically active even-parity HH-excitons are denoted as capital letters, $A : [1,3]^h$, $B : [2,2]^h$. Channels of LH-excitons are as small letters, $c : [1,2]^l$, $f : [2,1]^l$, and those of odd-parity HH-excitons are as primed small letters, $b' : [1,2]^h$, $d' : [2,1]^h$, $e' : [1,4]^h$. Solids lines with labels of FR states stand for results calculated with valence-band mixing. Dashed lines with parenthesized labels of FR states are for results calculated without it for comparison. $A1$, $B2$, etc. mean the $1s$-state of A, the $2s$-state of B, and so on.

Finally, the WSL driven by far infrared cw-laser and an associated excitonic effect are considered. Here this laser induces intraband transitions between WSL subband states. This is termed the dynamic WSL (DWSL). As for electronic states of a free carrier in the DWSL, these can be analyzed in terms of the Floquet theorem because of temporal periodicity of the system concerned. The electronic structure resulting from such optical non-linearity indicates quasi-energy band formation and band collapse, depending on strength of this applied laser field F, as is shown in Fig. 3(a) for 4.5nm-GaAs/4.5nm-$Al_{0.3}Ga_{0.7}$As-superlattices with $F_0 = 10$ kV/m. These phenomena akin to the Autler-Townes splitting are interpreted in terms of dynamic delocalization (DDL) and dynamic localization (DL) of the carrier,

respectively [7]. Both DDL and DL are caused by photon-assisted tunneling between adjacent subband states coupled by the intraband transitions. Next the excitonic effect that is significant in a real system is introduced into the DWSL. An electron-hole pair concerned here manifests itself as a dressed exciton, and the associated quasi-energy structure is altered, as is seen in Fig. 3(b). Specifically, it is seen that the energy structure for DL is blurred to some extent due to the excitonic effects. Examining FR absorption spectra of exciton DWSL by irradiating another weak probe laser, it is found that the spectral intensity and profile vary drastically at F tuned to the position of DL from those corresponding to DDL. Moreover, binding energies of the dressed excitons are notably changed from those of WSL excitons with $F = 0$. More detailed investigations of the exciton DWSL are in progress, resorting to the semiconductor Bloch equations for FWM spectroscopy with arranging three laser pulses.
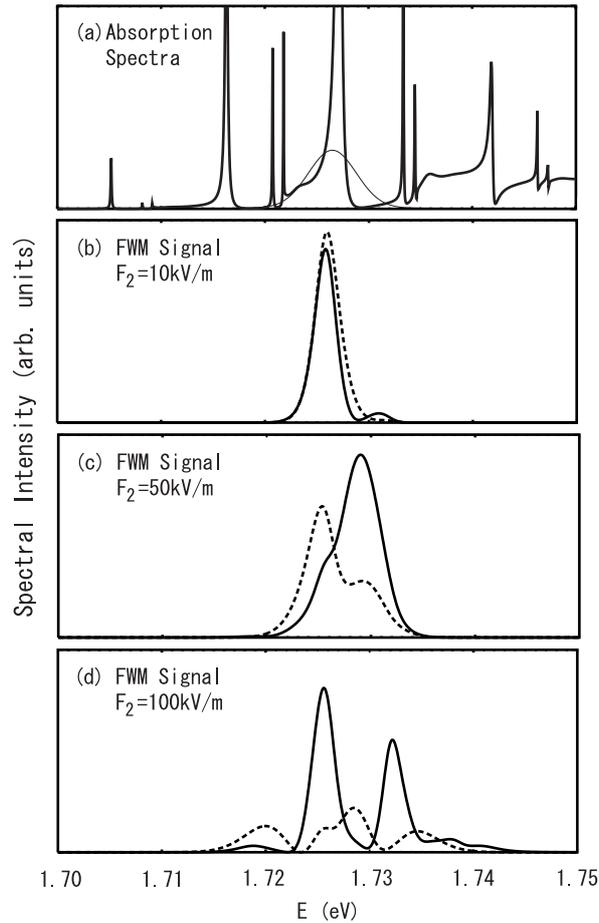
Figure 2: (a) Linear absorption spectra of exciton FR states in 3.4nm-GaAs/1.7nm-Al$_{0.3}$Ga$_{0.7}$As-superlattices with a biased dc-electric field F_0 =25 kV/m as a functions of photon energy E. (b) FWM spectra (power spectra of time-resolved FWM signals) for the WSL exciton FR versus E, where a peak amplitude of the probe pulse laser F_1 =1 kV/m, that of the pump laser pulse F_2 =10 kV/m, and F_0 =25 kV/m, respectively. Here temporal pulse widths of both lasers is set 500 fs, dephasing time and population relaxation time are given by 400 fs, and the time delay of the two-pulse irradiation is 0 fs. The solid line represents the FWM signal obtained by full calculations including the pump laser-exciton interaction and the many-body exciton-exciton exchange-interaction, while the dotted line means that without the latter. Spectral distribution of the pulses are depicted as a bell-shaped curve denoted by a thin line in (a), where the 1s state of the WSL index $\nu = 0$ is selectively excited. (c) Same as (b) but F_2 =50 kV/m. (d) Same as (b) but F_2 =100 kV/m.
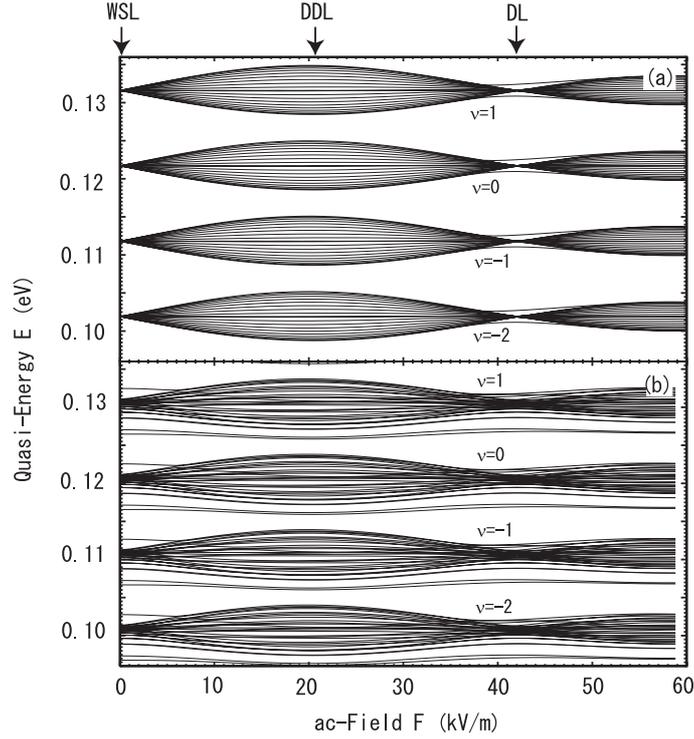
Figure 3: Quasi-energies E of DWSL as functions of applied cw-laser field F in 4.5nm-GaAs/4.5nm-$Al_{0.3}Ga_{0.7}$As-superlattices with a biased dc-electric field F_0 =12 kV/m. Frequency of the laser coincides with the Bloch frequency of the system. Here E is reckoned from the bottom of the conduction band of GaAs. The label of ν denotes the WSL index associated with an energy level at F=0, where $\nu = 0$ means the parent band and other indices represent photon side bands (replica). Positions of F relevant to WSL, DDL, and DL are indicated at the top of the figure. (a) DWSL without excitonic effects. (b) DWSL with excitonic effects.

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Chemistry Derived by Electron Impact to Individual Molecules Adsorbed on Metal Surfaces

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Scanning tunneling microscope (STM) is a valuable tool to handle single molecules adsorbed on conductive surfaces, giving a high potential to vibrationally excite individual molecules to highly excited states.   Here we demonstrate following phenomena that we have been able to handle;

1.   Electron stimulated migration (ESM) for CO, which is initiated by the excitation of a high-frequency (HF) vibrational mode (C-O stretching mode).   A theoretical model, which is based on the anharmonic coupling between low-frequency modes (the hindered-translational mode related to the lateral hopping) and the HF mode combined with electron-hole pair excitation, can explain why the hopping of CO is observed on Pd(110) but not on Cu(110).

2.   Dehydrogenation of trans-2-butene single molecule to 1,3-butadiene through multiple excitation.

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Diffuse Excess Electron States

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Unusual anions result when excess electrons become trapped outside the nuclear frameworks of neutral molecules or clusters by electrostatic fields originating from those frameworks. The excess electrons in such anions are typically loosely-bound and spatially-diffuse. Here, we report on our anion photoelectron spectroscopic studies of two types of electrostatically-bound, diffuse excess electron states.

Anions in which the excess electrons are bound predominantly by dipolar fields are commonly referred to as 'dipole bound anions'. We have studied many examples, including $(H_2O)_2^-$, $CH_3CN(H_2O)^-$, $(HF)_2^-$, $(HF)_3^-$, $Indole(H_2O)_n^-$, $HCl(H_2O)_n^-$, $HCN(H_2O)_n^-$, molecular nucleic acid base anions, and anions of zwitterionic amino acids. In all of these cases, dipole binding exhibits a distinctive, photoelectron spectral signature. Several selected studies will be highlighted. In the case of $(HF)_3^-$, we and our theoretical collaborators found evidence not only for dipole binding between a chain of HF molecules and an excess electron, but also for dipole binding in which both a single HF molecule and a hydrogen fluoride dimer were separately bound to the same excess electron [1]. In the case of uracil, we found that, while its molecular anion is dipole bound, its hydrated anionic form is a conventional, valence anion, illustrating

competition between the two types of electron binding. In the case of amino acids, we relied on the appearance of a dipole bound spectral fingerprint to signal the advent of penta-hydrated glycine's zwitterion. Additional related topics include the close relationship between dipole binding and the formation of solvated electrons and the possibility that quadrupole-bound anions may exist.

Molecular Rydberg radicals are examples of net neutral species in which excess electrons are bound by electrostatic monopolar fields, i.e., by cations. We have found several ammonium-based examples of anions of Rydberg radicals, these being NH_4^-, $N_2H_7^-$, $N_3H_{10}^-$, $N_4H_{13}^-$, $N_5H_{16}^-$ and, in some cases, their solvated complexes [2]. All of these exhibit photoelectron spectral signatures which are suggestive of extremely diffuse excess electron states. In part, because theory [3] finds the excess electron's spatial distribution to be Rydberg-like, these species are commonly referred to as 'double Rydberg anions'.

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Theory of low-energy electron attachment to molecules and clusters

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Low-energy electron attachment to molecules typically goes through formation of a temporary negative-ion state. The excess energy might be released then in the form of kinetic energy of neutral and anionic fragments. In this case we have a dissociative attachment (DA) process. In large systems, like polyatomic molecules and clusters, the temporary negative ion can be stabilized by coupling of electron motion with vibrational degrees of freedom (or electron-phonon coupling). The DA case has been relatively well studied theoretically, although completely ab initio calculations are still available only for diatomics. The second (nondissociative) case is much more challenging to the theory. However, some features of this process can be understood by using model appoaches.

For theoretical description of DA processes we use the resonance R-matrix theory [1] which allows us to obtain DA cross sections in terms of few parameters, the R-matrix pole and the surface amplitude as functions of the internuclear separation. These parameters are adjusted to reproduce experimental or ab initio data on other resonance processes, e.g., resonance elastic scattering or vibrational excitation.

The following important features in DA have been investigated by this method:

1. Vibrational Feshbach resonances [2,3]. These resonances occur due to a temporary capture of the incident electron by the long-range field of a vibrationally excited molecule. Very pronounced vibrational Feshbach resonance was detected experimentally in methyl iodide [2] below the first threshold for excitation of the symmetric stretch vibrations. Higher thresholds are free of the resonances but exhibit pronounced threshold cusps.

2. Low-energy behavior of exothermic DA. This behavior is controlled by the long-range interaction between the incident electron and the target molecule. For non-polar molecules the energy dependence is given by the Wigner law which should be modified in the case of polar targets. The absolute value of the cross

section is often consistent with the Vogt-Wannier [4] or extended Vogt-Wannier [5] theory for the capture of a charged particle into a polarization well.

3. The temperature dependence of the DA cross sections. This dependence is particularly strong in methyl chloride and methyl bromide [3].

4. The influence of environment, particularly surface and condensed matter effects in DA [6].

In case of electron attachment to clusters we have been concentrating on studies of the influence of the cluster environment on vibrational Feshbach resonances. For CO_2 and N_2O clusters the polarization interaction between the electron and the cluster leads to a red shift in the resonance position [7] but the resonance width does not change substantially. In contrast, cross sections for DA to methyl iodide dimers and trimers exhibit substantial broadening of the vibrational Feshbach resonance [8]. This effect can be successfully described by the resonance R-matrix theory which takes into account a modification of the long-range part of the electron-molecule interaction due to the cluster environment.

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Effects of rotation and Jahn-Teller coupling on H3+ dissociative recombination

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The enigmatic problem of describing the dissociative recombination (DR) of H3+ ions by low energy incident electrons has withstood more than a decade of serious theoretical efforts. Progress made a year ago[1] pointed out a new mechanism that apparently controls this DR process, namely Jahn-Teller coupling between the incident electron and the molecular ion. At the workshop, I will discuss a full calculation that combines multichannel quantum defect theory (MQDT) implemented at the first principles level, a hyperspherical coordinate method to include all three dimensions of vibrational motion, and the quantized rotational level structure of the target ion. A new implementation of the molecular MQDT calculation, using vibrational channel functions that obey Siegert (outgoing wave) boundary conditions, permits a simple extraction of the dissociative probability flux. The results show quantitative agreement with the average DR rate coefficient measured in the newest Stockholm storage   ring experiment, although the detailed predictions of individual features show discrepancies with experiment that have not yet been resolved.

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Dissociative Excitation of Molecules in Photonic and Electronic Collisions. Formation and Dissociation Dynamics of Molecular Superexcited States.

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Abstract

A survey is given of recent progress in experimental studies of the dissociative excitation of molecules in photonic and electronic collisions with molecules in the excitation-energy range of 10-50 eV with a particular emphasis placed on the formation and dissociation dynamics of molecular superexcited states which have been recently substantiated experimentally.   In photonic collision experiments synchrotron radiation as an excitation photon source combined with newly developed coincidence or two-dimensional spectroscopy-techniques have been used for studying optically allowed superexcited states, while in electronic collision experiments newly developed coincident electron energy-loss spectroscopy has been used for studying optically forbidden superexcited states. Molecules studied are ranged from simple diatomic and triatomic molecules to polyatomic molecules such as hydrocarbons. Most of the observed superexcited states are high Rydberg states which are vibrationally (or/and rotationally), doubly, or inner-core excited and converge to each of ion states. Non-Rydberg superexcited states are also observed. Dissociation into neutral fragments in comparison with ionization is of unexpectedly great importance in the observed decay of each of these states. Dissociation dynamics as well as its products are remarkably different from those for lower excited states below about ionization thresholds. These experimental results have motivated much new developments of theoretical investigations of molecular superexcited states and their dissociation

dynamics as well as of optical oscillator strength distributions. Some remarks are also presented of superexcited states as collision complex in electron-ion recombination, electron attachment, and Penning ionization processes. As related perspectives, comments are presented on an important role of molecular superexcited states in phenomena in ionized gases and further on these states in the condensed phase.

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Resonant vibrational excitation of CO_2 by electron impact: Nuclear dynamics on the coupled components of the $^2\Pi_u$ resonance

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Although the principal features of low-energy electron-CO_2 scattering have been the subject of numerous experimental and theoretical investigations, recent laboratory studies[1] of resonant vibrational excitation have been carried out with unprecedented energy resolution and have revealed subtle details in the excitation cross sections whose origin and quantitative understanding pose serious challenges for *ab initio* theory.

The electron-CO_2 system is complicated for a number of reasons. The phenomenon of 'Fermi resonance', ie. an accidental degeneracy that occurs between certain zero-order vibrational states, leads to strong mixing between vibrational modes and necessitates a multi-dimensional treatment of the nuclear dynamics. The problem is further complicated by the fact that the negative ion "shape" resonance, which is degenerate in linear geometries ($^2\Pi_u$), splits into two non-degenerate surfaces upon bending which are strongly coupled by non-adiabatic Coriolis effects (Renner-Teller coupling).

I will describe the results of a fully *ab initio* study of resonant vibrational excitation of CO_2 by electron impact via the 3.8 eV "$^2\Pi_u$" shape resonance. The fixed-nuclei, electronic scattering problem is first solved, using the complex Kohn variational method, for a variety of symmetric-stretch geometries and for a range of bending angles. The fixed-nuclei cross sections are then analyzed to produce resonance parameters for both the $^2A_1$ and $^2B_1$ components of the resonance which, in linear geometry, correspond to the two components of the doubly degenerate $^2\Pi_u$ state of CO_2^-. The nuclear dynamics problem is solved by carrying out two-mode, time-dependent wavepacket studies on the coupled resonance surfaces in a complex local potential or 'boomerang' model.

These calculations have produced vibrational excitation cross sections that are in excellent agreement with experiment and reveal the origin of the subtle interference effects observed in the most recent experimental studies. To our knowledge, this represents the first time that all aspects of an electron-polyatomic collision, including not only the determination of the fixed-nuclei electronic cross sections, but also a treatment of the nuclear dynamics in multiple dimensions on coupled resonance surfaces, has been carried out entirely from first principles.

Cross sections for excitation of the [(2,0,0)/(1,2,0)/(0,4,0)] Fermi triad in CO_2 by electron impact. *Ab initio* results are compared with recent experiment.

Fermi Triad -- SCF ground state
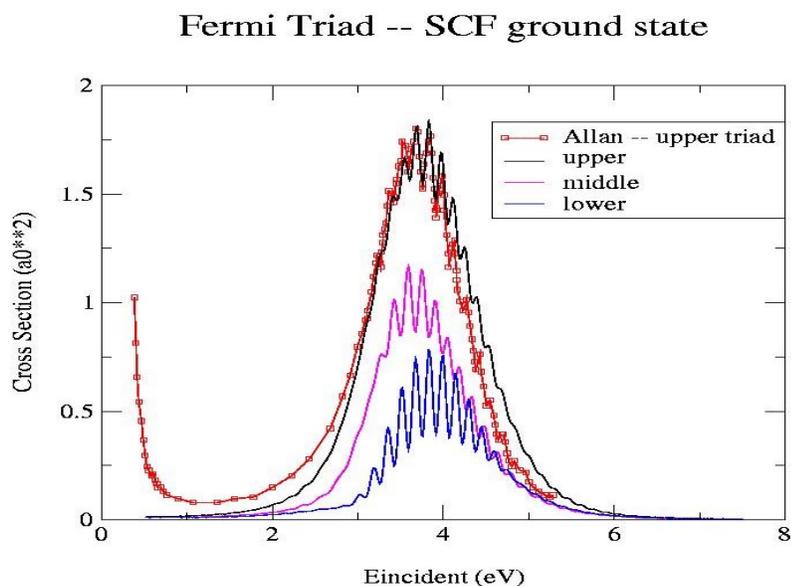
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Nonadiabatic Transitions and Resonances in Chemical Reaction Dynamics

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abstract:Nonadiabatic transitions and various types of resonances in simple chemical reactions will be discussed. In addition to the conventional types of resonances, there are some peculiar ones such as those assisted by vibrationally nonadiabatic transitions and the resonane tunneling. The interesting phenomenon of complete refelction in one-dimensional system will also be briefly touched upon.

Photo double excitation of helium in a strong DC electric field

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The study of doubly-excited states of helium has long been used as a sensitive test of the understanding of electron correlations. Synchrotron radiation provides a high resolution source of photons in the energy range required for excitation of these states, which is inaccessible using laser sources. To date, studies of the influence of a high electric field on the behaviour of doubly excited states have been limited, and a new apparatus has been constructed which allows fields of up to 90 kV/cm to be applied to the interaction region where the states are formed.

Photons from beamlines at both the Photon Factory and the Advanced Light Source, Berkeley, have been used to study doubly-excited autoionising states of helium in a high electric field. The states appear as resonances in the detected ion yield, metastable yield and photon decay spectra. Initial experiments at the Photon Factory showed prominent effects due to Stark shifting and mixing of the resonances observed in the ion yield spectrum. The evolution of the states as a function of the field strength was, however, quite different to that predicted by a recent theoretical calculation [1]. The extremely high resolution at the ALS allowed a detailed investigation of these effects to be commenced. Application of novel techniques, taking advantage of the time structure of the synchrotron radiation, has allowed the separation of the photon decay and metastable yield channels. The doubly excited resonances have thus been able to be observed in 3 different decay channels, allowing further insight into the structure of these states and their behaviour in a strong electric field.

Experiments have recently been extended to investigate the Stark effects on singly and doubly excited states in neon, above the first ionisation threshold, and some progress has been made in describing the bevahiour of these states as the field in the interaction region is varied.

Results will be presented for helium and, if time permits, neon. Detailed comparison with available theory will be made and further studies proposed for these systems.

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Negative ion resonances and radiation damage in biological targets.

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A significant fraction of the energy imparted to condensed matter from high-energy radiation is transferred via the production of secondary electrons with initial energies < 20 eV [1]. Prior to their thermalization, secondary electrons interact with the condensed medium in which they were generated. As a consequence, there is a need to investigate the condensed phase interactions of low energy electrons (LEE) and so identify their role in radiation damage to living systems. Such studies are possible using energy-selected LEE beams incident from vacuum upon thin solid film targets.

Experiments of this type on simple molecular solids have revealed that, as in the gas phase, scattering cross sections at low energies are dominated by the formation of negative ion resonances (i.e., short-lived anionic states) which can induced molecular damage by their decay into the dissociative electron attachment (DEA) channel or that of dissociating electronically excited states [2]. In recent years, these studies have begun to focus on biomolecular targets, including molecular DNA, which has been shown to be surprisingly susceptible to electron damage via resonances [3].

In this contribution, we will describe recent LEE impact experiments on thin films of biomolecules including water ice, plasmid DNA, deoxyribose analogues, DNA bases, protein sub-units and self-assembled monolayer films of short single strands of DNA. The energy dependence of the yields of various fragments induced by LEE impact on these compounds exhibit strong variations which are due to the formation of negative ion resonances. These experiments allow us to compare the variation in the yields of single and double strand breaks of the DNA backbone, to the desorption of anions following electron impact on pure samples of the DNA sub-units listed above. Furthermore, desorption experiments with single-stranded DNA, indicate that dissociation via transient anionic states produces neutral fragments, the yields of which are sensitive to the base identity and sequence in the oligonucliotide.

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Coupling between dipole-bound and valence states: the Nitromethane anion

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Nitromethane is a prototypical example for a polar molecule that can bind excess electrons in two fundamentally different ways. On the one hand, dipole-bound anions can be formed where the extra electron is essentially attached to the electrostatic dipole potential of the neutral system. The associated binding energies are small, and the dipole-bound electron occupies an extremely diffuse orbital. On the other hand, the extra electron can occupy a compact valence orbital, and a stable, conventional or valence anion with a notably changed equilibrium structure is formed.
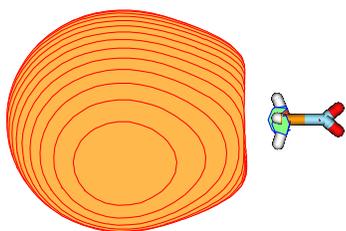
Dipole-bound state   Valence state
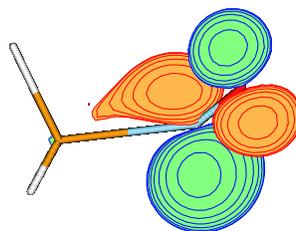
The classification of these electronic states as dipole-bound or valence does in fact suggest a diabatic viewpoint, and we investigate the coupling

1

between these two electronic states of the nitromethane anion. The electronic coupling element W is extracted from a one-dimensional cut through the two lowest adiabatic potential energy surfaces by fitting of a simple avoided crossing model potential. In other words, W is effectively approximated as half the smallest splitting.

Aiming for high level ab initio calculations of the two states along the cut, there are two important questions: how can one achieve a reasonably balanced description, and how should one include the region where the upper adiabatic state is a resonance? Regarding the former issue, it is essential to include electron correlation effects at a high level, and we discuss how a balance between the two very different electronic states can be achieved using either configuration interaction or propagator based methods. In the second place, the autodetachment lifetime following vertical electron attachment to the neutral is computed, but the calculation of the resonance state turns out to be very expensive, and so far, we include the second adiabatic state only at geometries where it lies below the neutral potential energy surfaces.

We find a coupling matrix element of 30 meV. On the one hand, this value is much smaller than the vertical excitation energies underlining the need for a diabatic picture. On the other hand, this value suggests rapid transitions on a mass spectrometric timescale substantiating the notion that the dipole bound state provides an efficient doorway for attachment to the valence state.

2

Dissociative Electron Attachment of Water and the Relevance to Environmental and Biological Issues

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Abstract

It is well recognized that high-energy particles, such as γ-rays, lose energy primarily via ionization and excitation of the target media. This produces a large number of low-energy (1-100 eV) secondary electrons which undergo both elastic and inelastic scattering events. A particularly important inelastic loss process involves the resonant capture of an electron to form a transient negative ion (TNI). A TNI can decay either via electron auto-detachment or dissociative electron attachment (DEA). DEA typically involves multi-electron resonances consisting of an excess electron bound temporarily to an electronically excited molecule. These core excited Feshbach resonances have lifetimes of $\sim 10^{(-12)} - 10^{(-14)}$ sec and can dissociate into stable negative ion and neutral fragments.

Water is ubiquitous and is present at many environmental surfaces and interfaces. Understanding the inelastic scattering of electrons with adsorbed water is important since DEA can contribute to safety issues associated with the storage of radionuclides and radioactive waste materials [1]. This is related to i) the presence of a large number of low-energy (1-10 eV) secondary electrons at nuclear material-oxide interfaces, ii.) the fact that DEA of water on oxide surfaces can have cross sections larger than the gas-phase value and iii.) DEA resonances in condensed water can result in the production of molecular hydrogen either directly or via the reactive scattering of the H^{-} fragment. Water is also a major component of all biological systems. In fact, radiation damage of DNA has received a large amount of attention, and it is now well established that single- and double-strand breaks result from both direct and indirect processes. The direct processes involve ionization of the DNA itself (primarily the base pairs), whereas the

indirect effect involves reactions with the ionization and excitation products of the surrounding "environment". This environment can be a protein or tightly bound "inner" and weakly bound "outer" waters of hydration. It is currently believed that the reactions of OH radicals (produced from these waters of hydration) lead to DNA damage. However, recent evidence strongly suggests that DNA damage also results from the interaction of low-energy electrons and involves DEA resonances of water and the intrinsic base pairs [2].

This talk will highlight some recent work on the DEA of interfacial thin films of water. In particular, I will discuss the low-energy electron stimulated desorption (ESD) of H^- (D^-) and H_2 (D_2) from nanoscale water films adsorbed on oxide surfaces and at biological interfaces Three low-energy peaks are observed in the ESD yields of H^- which are identified as arising from excitation of the $^2B_1$, $^2A_1$, and $^2B_2$ DEA resonances [3,4] of water. Additional structure is observed between 18 and 32 eV, which may be due to ion-pair formation or DEA resonances involving the $^2A_1$ level [3,4]. The peak positions of the $^2B_1$, $^2A_1$, and $^2B_2$ resonances shift slightly to lower energy, and the ion yields increase with the thickness, temperature and morphology (local order) of the water films. These results have been discussed in terms of the local positions and configurations of the interfacial water molecules, narrowing of bandwidths and increased excited state lifetime effects. We have also used laser resonance-enhanced multiphoton ionization to monitor the translational, vibrational and rotational state distributions of the departing hydrogen molecules. We observed structure between 8-16 eV and 18-32 eV in the yield of H_2 (D_2) ($^1\Sigma_g^+$, ν =0-2, J=0-3) which we attribute to the formation of core excited negative ion resonances [5,6]. These resonances, or the excited states produced by autodetachment, decay via a molecular elimination step to yield H_2 ($^1\Sigma_g^+$) directly. The relevance of these detailed DEA studies of interfacial water to the environmental and biological issues mentioned above will be emphasized.

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Aspects of Adiabaticity in an Atomic BEC

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The successful generation of trapped atomic Bose-Einstein condensates in laboratories[1] has opened a new domain of atomic and optical physics, and challenging phenomena continue to be reported regularly through international journals. Theoretical studies of the phenomena, however, are traditionally based on the mean-field theory due to Bogoliubov[2], which was later extended by Gross and Pitaevskii[3] into the celebrated GP equation, whose basic premise is that the system behaves as a blob of matter representable by a field. This picture has proven so remarkably successful that most observed phenomena are indeed largely accountable by this equation, and conversely no theory thus far has been developed tangentially to this view. Despite all the success, there is one aspect of the BEC to which no complete treatment, to my knowledge, has been given, that is the free expansion used by experimentalists to achieve the optically resolvable image size of a BEC. Our investigation begins with the mystery that at least the density profile of a BEC remains intact during its expansion, inclusive of even the lattice structure of quantized vortices[4]; it suggests that some invariants, possibly adiabatic, might exist. In part, such an expectation is supported by the hyperspherical works of reference [5] and of [6]. Departing from the field theoretic picture, or rather from the independent particle representation, suffers serious and technically insurmountable disadvantages owing to the sheer number of particles involved. Our discussions to follow will thus keep the field-theoretic language and treatment closely in mind, though the pursuit of invariants, if any, naturally favors the framework based on the invariants themselves. As a specific candidate, we take the hyperradius, namely the effective size of the system, which corresponds to the well-defined optical image size when the system is expanded. Close to the ground state, this parameter's comportment suggests its connection with the single particle excitations. Anyhow, well-known from classical mechanics, this variable emerges in the context of the virial theorem, and is closely related to the uncertainty principle.

There seem to exist two working definitions of the hyperradius, each pertaining to a specific physical limit. One is the standard definition as employed in references [5] and [6] suitable for representation of single-particle excitations, and the other the local mean-square radius of the GP ground state solution pertinent to the evolution of collective modes. Leaving the details to the meeting, I wish to summarize highlights of our preliminary investigation.

1) The hyperspherical single-channel zero-th order approximation accounts for the monopole, dipole, and quadrupole excitations once the trap's isotropy is broken even infinitesimally.

2) The coupled GP equation for single-particle excitations may be solved by the adiabatic diagonalization method. Thus introduced are the local creation and annihilation operators. The hyperspherical single-channel zero-th order approximation yields the single-particle wave functions of low-energy excitation whose rough features resemble those of the GP solutions.

3) Collective oscillations as well as free-expansion of the BEC gas proceed largely adiabatically with respect to the local-mean square radius of the GP ground state solution so that the local particle density is a function of this single parameter. The wavepacket then retains its minimum uncertainty character. The retrieval of the phase should require additional, but not terribly strenuous, effort.

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Couplings in the Continuum

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When two or more electronic resonances of the same symmetry are close together in energy, electronic coupling between the resonances can occur. Because the states are chosen to be the adiabatic eigenstates of H_{el}, the resonant states can interact with each other, in second order, via the electron scattering continuum into which the resonances can decay. The process is described as follows: an electron is captured into a resonant state. During dissociation, the electron makes a 'virtual' transition from the original resonance to the continuum, and then makes a second 'virtual' transition from the continuum to a second resonance state, which will dissociate into stable products. These resonant states are coupled by the same potential, which is responsible for the finite auto detachment lifetimes of isolated molecular negative-ion states [1].

This mechanism was first used by Hazi [1] to describe dissociative electron attachment to HBr. In dissociative attachment this is not a common situation since there are usually a small number of resonant states. In contrast, in the case of dissociative recombination, there exist core-excited resonance states which form a Rydberg series converging to excited states of the ion that have the same symmetry. We will present the first application of this mechanism for the case of dissociative recombination specifically to the system HeH^+.

Larson and Orel [2] reported calculated total cross sections and product state distributions for the dissociative recombination of HeH^+ with electrons in the high-energy resonance region. They compared several models for the non-adiabatic coupling, and were able to predict total cross section values that agreed with the experimental values. However, the prediction for the product state distributions did not agree with experiment. The redistribution of flux between the various channels due to this mechanism and its effect will be discussed.

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Interaction between virtual states and resonance states in electron-polyatomic collisions

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We interpret the resonances in low-energy electron-polyatomic scattering with the help of a two-channel analytically solvable model. The model, which treats two partial-wave Hamiltonians with different l values coupled by a long range dipole interaction, is a generalization of similar single-channel models that have previously been used to interpret the low-energy behaviour of electron scattering by polar molecules.

The model allows us to study the effect of bending and stretching on both resonances and virtual states. We do this by tracking the poles of S-matrix in the complex k-plane as a function of bend and stretch.

The connection between resonant and virtual states is found to display a different topology in the case of a polyatomic molecule than it does in diatomic molecules. In a polyatomic molecule, these states1 may have a conical intersection and consequently acquire a Berry phase along a closed path in the two-dimensional vibrational motion.

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Vibrational excitation of a carbon dioxide molecule by electron and positron impacts

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An electron (e^-) or a positron (e^+) collision process with a molecule gives us fundamental information of scattering dynamics, relevant to condensed matter physics, radiation physics and so forth. From the point of view of elementary physics, e^-–molecule and e^+–molecule collisions are worth studying not only independently but comparatively as well. In e^- (e^+) scattering from a molecule, one of the important inelastic processes is vibrational excitation, which is the dominant energy loss process of an incident particle below 10 eV. Carbon dioxide (CO_2) is an interesting molecule as a target of the e^- (e^+) collision, since it is one of the simplest polyatomic molecules with the symmetry of $D_{\infty h}$ and the problem of e^-–CO_2 collisions is important for various applications, e.g., planetary atmospheres, plasma chemistry, etc. In the present talk, vibrational excitation of the CO_2 molecule in collision with e^- and e^+ is studied theoretically. The range of incident energy is $2 \leq E \leq 10$ eV for e^- and $2 \leq E \leq 6$ eV for e^+ (it should be noticed that the threshold of positronium formation is 6.7 eV). Each fundamental mode of vibration is treated separately. Main part of this talk and related topics have already been given in [1–3].

CO_2 has three fundamental modes of vibration. The ground state of CO_2 for vibration is denoted as (000) and the lowest excited state of each mode is described as (100) for symmetric stretching, (010) for bending and (001) for antisymmetric stretching. In the present calculation, scattering dynamics is treated by the vibrational close coupling method for each excitation from the ground state to the lowest excited state within the fixed nuclear orientation approximation. In the interaction potential for the e^-–CO_2 collision system, the static and correlation-polarization terms are attractive and an attractive electron-exchange term, which plays an important role in low energy e^- scattering, is also added. On the other hand, the interaction for e^+ impact consists of repulsive static and attractive correlation-polarization potentials and includes no electron-exchange term. As a result, the three attractive interactions are summed up for e^- impact and the repulsive static interaction and the attractive correlation-polarization interaction cancel out each other to a large extent for e^+ impact.

Figure 1 shows the integral cross sections for the excitation of (000) $\rightarrow$ (100) by e^- impact and e^+ impact. The present e^+ impact cross section is compared with the theoretical result obtained by Gianturco and Mukherjee [4] (they treated symmetric stretching mode of vibration only). Although the present e^+ impact cross section is somewhat smaller than that of Gianturco and Mukherjee, the energy dependence of the two data sets are qualitatively similar. The quantitative disagreement between these cross sections is considered to be due to the difference in the accuracy of the molecular wave function used to obtain the interaction potential. It is also noticed that the number of excited states of vibration included for close coupling calculation is 1 in the present calculation and 4

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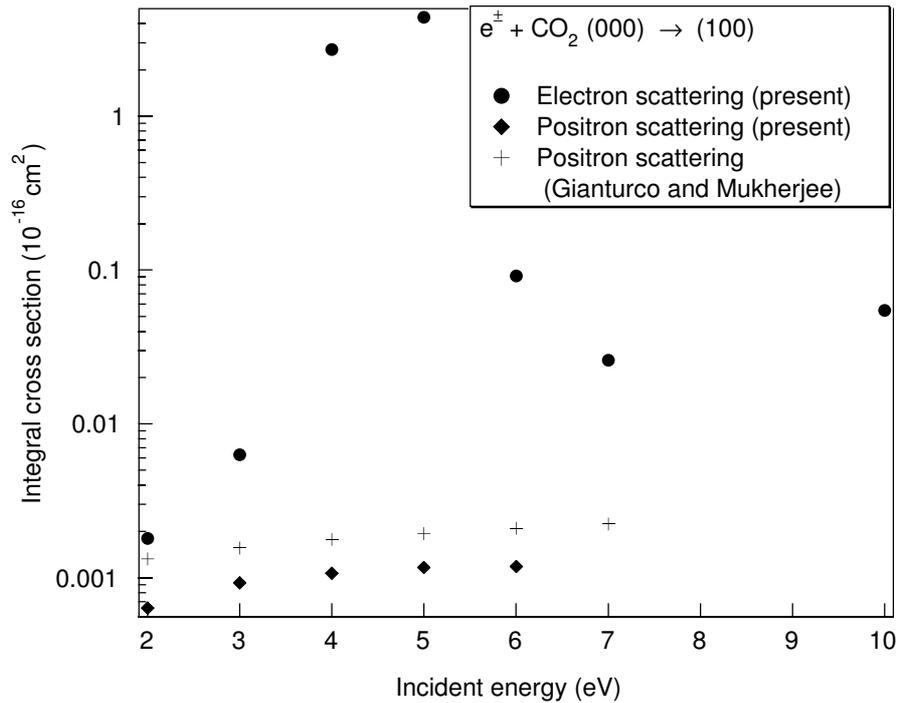
Figure 1. Integral cross sections in units of 10^{-16}cm^2 for $(000) \rightarrow (100)$ excitation of CO_2 by e^- impact and e^+ impact. The present result of e^+ impact is compared with the theoretical result obtained by Gianturco and Mukherjee [4].

in that of Ref. [4]. In the present data of e^- collision, the strong Π_u resonance peak is seen at around 5 eV and no such structure exists in the e^+ collision cross section. The difference of the interactions between the collisions by e^- and e^+ described above results in the different energy dependence of the cross sections.

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Resonances in Low-energy Positron Scattering from Atoms and Molecules [+]

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Although ubiquitous in electron scattering, resonances in elastic and inelastic cross sections for positrons have been more elusive. This paper will discuss recent progress made using a high-resolution (i.e. 25 meV, FWHM) positron beam [1] to search for comparable resonances in low energy positron scattering from atoms and molecules.

This work was done using a beam of positrons extruded from a Penning-Malmberg trap with a well-defined energy. The positrons are magnetically guided through a gas cell, and the intensity and energy distribution of the transmitted beam is measured using a retarding potential analyzer. A new analysis technique allows us to distinguish elastic and inelastic scattering processes by exploiting our ability to have different magnetic field strengths in the scattering and analysis regions. [2]

In this talk, I will discuss the current status of resonance searches in low energy positron scattering. To date we have observed no sharp resonance in positron total cross sections [3], even though their existence has been predicted by a number of calculations. [4] However, we have observed sharp onsets at threshold in several inelastic cross sections. A sharp rise near threshold is observed in the vibrational excitation cross sections of all of the molecules we have studied including CO, CO_2, and H_2. [5] These sharp onsets are also present in some of the electronic excitation measurements. In particular, in N_2 there is a peak in the positron scattering near threshold that is not present in comparable electron data. [6]

An increase in our beam resolution and improved ability to look at lower energy positron interactions would help us develop a clearer picture of this and other resonance behavior. Some improvements to the current setup towards this goal will be discussed. Also other likely candidates for resonances will be discussed, including a possible resonance in the total cross section at the threshold of Ps(n=2) state. [7]

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The Role of Resonances in Molecular Rydberg States

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Molecular Rydberg states play an important role in a variety of collision processes. Recently the interest to molecular Rydberg states has increased due to theoretical prediction [1] that a certain class of molecular Rydberg states formed by interaction of a Rydberg atom with a ground-state Rb atom can be stable at very large internuclear separation, comparable to the size of the Rydberg atoms.

The properties of low-energy electron scattering by alkali-metal atoms are crucial for formation of such dimers. There are two distinct features: a virtual ^{3}S state and a ^{3}P shape resonance [2]. The ^{3}S and ^{3}P resonances lead to formation of local minima supporting localized vibrational states. The ^{3}S-dominated states were termed trilobite states [1] due to specific shapes of their wavefunctions.

In the present work [4], we use the Kirchhoff integral method [3] to calculate properties of the A*-B system, where A* is a Rydberg atom and B is a ground state alkali-metal atom. The e+A$^+$ interaction is included using Coulomb's Green function with the quantum defects. Interaction of the Rydberg electron with atom B is presented by a pseudopotential, which reproduces correct phase shifts from the Dirac R-matrix calculations and binding energies for corresponding negative ion. Analytical formulas for the wavefunction and dipole moment of trilobite state were derived. The obtained potential energy curves can be employed for calculation of inelastic processes in A-B collisions and for calculations of properties of long-range molecular Rydberg states. One of their most important features are dipole moments which appear due to orientation of Rydberg atom A in the presence of perturber B.

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Charge-Asymmetric Coulomb Explosion of Diatomic Molecules in Intense Laser Fields

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Much attention has been recently called to the interweaved electronic and nuclear dynamics of a molecule in intense ($\sim 10^{15}$W/cm^2), short pulse ($\sim 10^{-13}$s) laser fields [1]. Of particular interest is the effect of *enhanced ionization*, i.e. ionization rate being much larger than that for the constituent atoms, basically caused by electron localization due to the intra-molecular barrier while the bond distance stretches.

In this talk, we develop a simple model for sequential multiple ionization of diatomic molecules AB in intense laser fields. Modifying the *field-ionization, Coulomb explosion* model by Posthumus *et al.*[2], we incorporate asymmetric charge states $q_A \neq q_B$ in respective steps, where either the outermost electron localized at the atomic site A, or that at B, is ionized as $(q_A - 1, q_B) \to (q_A, q_B)$, or as $(q_A, q_B - 1) \to (q_A, q_B)$. Furthermore, we take account of possible electron dynamics due to the oscillating field: nonadiabatic excitation of a localized electron associated with the inner saddle point, and subsequent field ionization associated with the outer saddle point in both directions according to the oscillating phase. It turns out as a consequence that, for a given net charge $q = q_A + q_B$, the larger the charge asymmetry $|q_A - q_B|$, the smaller the bond distance R_{ion} at which ionization occurs.

The present model is shown to account for the behaviors observed in different molecules such as N$_2$ [3] and NO [4] through the kinetic energy release in Coulomb explosion, as follows. 1) While increasing with q, the distance of ionization oscillates with the even-odd effect in a symmetric pathway ($|q_A - q_B| = 0$ or 1). 2) Ionization occurs earlier in asymmetric channels than in symmetric ones among competing pathways as $R_{ion}(21 \to 31) < R_{ion}(21 \to 22)$.

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Resonance Charge Transfer in Dipole Bound Anions
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Any molecule with a dipole moment above ~2.5 Debye can form a stable negative ion (dipole-bound anion).[1,2] These anions are best produced by "resonance" charge exchange from atoms in high Rydberg states (Rydberg electron transfer, RET). RET to form dipole-bound anions occurs over a narrow range of effective principle quantum number, n^*. We have studied dipole-bound anions for over 25 molecules with dipole moments between 2.5 and 5.5 Debye. The excess electron in such an anion is very diffuse and weakly bound. Binding energies (electron affinities, EAs) are estimated from the narrow range of n^* at which charge exchange occurs and also from measurements of the electric field $E_{critical}$ required to detach the electron. Electron affinities range from less than ~1 milli electron volt (meV) to ~55 meV. Reactions of chiral Rydberg atoms (oriented atoms with selected M_J) with chiral molecules have been studied to examine enantiomeric selective charge exchange reactions.[3] Charge-exchange reactions between dipole-bound anions and polar molecules are also under investigation. These reactions can be thought of as electron exchange (i.e. "hopping") between polar molecules. The long-range nature of the electron-dipole interaction provides a mechanism for electron transport involving polar molecules. These studies have important biochemical implications such as in the electron transport chains found in biology.

We will also discuss our progress toward studies of photodetachment of dipole-bound anions. Intense beams of dipole-bound anions are produced by rubidium Rydberg atoms produced by resonantly enhanced two-photon excitation (5s $^2S_0 \rightarrow$ 6p $^2P_{1/2} \rightarrow$ n^2S, n^2D). A third laser is used to photodetach the weakly bound electron. Photoelectron spectroscopy is used to determine the electron affinity.

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FORMATION OF PROTONIUM IN COLLISIONS OF ANTIPROTONS WITH HYDROGEN

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When antiprotons are trapped they undergo atomic reactions with background gases which remove them from the trap. They may capture into bound states with subsequent annihilation by nuclear interactions. An understanding of these processes requires reliable cross sections for low-energy collisions of antiprotons with atoms.

We have used the advanced adiabatic theory to compute protonium formation and ionization for low energy impact of antiprotons on atomic hydrogen. The advanced adiabatic method derives from an exact Sturmian representation, given by Ovchinnikov and Macek[1], of the full wave function for three particles interacting via electrostatic interactions. For that reason it must include all reaction channels, including protonium channels even though no protonium wave functions are included in the basis set. Even in the one-Sturmian approximation, which is crucial to the advanced adiabatic theory, all physical channels are included.

The conventional adiabatic electron energies for an electron in the field of $p + \overline{p}$ in the separated atom limit are the Stark energy levels of the H-atom in the field of the antiproton. At some finite distance, called the Fermi-Teller radius $R_{\mathrm{FT}} = 0.693...$, the electron just becomes unbound in the finite dipole field of the $p, \overline{p}$ system. At the united atom limit, where the antiproton coincides with the proton, the electron nuclei potentials cancel and the electron is completely free. The ground state potential curves $\varepsilon(R)$ therefore move into the continuum with decreasing internuclear separation and the bound states become quasi-stationary states. An approximate expression for $\varepsilon(R)$ for R less than R_{FT} is

$$
\begin{aligned}
\varepsilon_{n_1 n_2 m}(R) &= \frac{4}{R^2}\left(\lambda_0(R) - \frac{7}{2}\right) \\
&- i\frac{4}{R^2}(2n_1 + m + 1)\sqrt{8\lambda_0(R) - \frac{49}{4}}
\end{aligned}
$$

with

$$
\lambda_0(R) = \left(n_2 + m + \frac{1}{2}\right)^2 - \frac{1}{2}\left(\frac{R}{n_2 + m + \frac{1}{2}}\right)^2,
$$

where $n_1 n_2 m$ are the parabolic quantum numbers of a hydrogen in a constant electric field.

The advanced adiabatic theory of employs the quantity $R(\varepsilon)$ inverse to $\varepsilon(R)$. This quantity is the solution of the equation $\varepsilon(R) = \varepsilon$. The advanced adiabatic theory should be more reliable at the lower energies where the relative velocities of the heavy particles become much smaller than the electron velocities. In
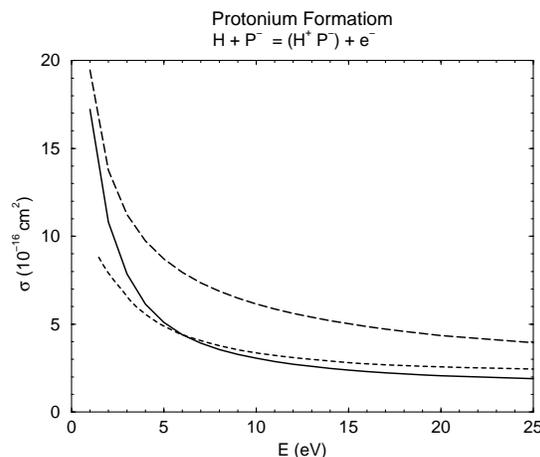
Figure 1: Cross sections for protonium formation. Short dash curve-CTMC from Schultz *et al*[2], long dash curve-upper limit orbiting cross section, solid curve-advanced adiabatic.

the region below the ionizaion threshold at 27.21 eV ionization occurs only by protronium formation. This allows a simple way to compute protonium formation in the advanced adiabatic theory, namely, we compute ionization without reference to the quantization of the protonium energies and then identify the cross section with protonium formation. This is convenient for computations of total protonium formation cross sections, but by using the $\frac{dE}{dn}$ energy interval weighting, n-distributions can also we obtained.

Figure 1 shows our protonium formation cross in the region below the ionization threshold at 27.21 eV. Also shown is the "upper limit" orbiting cross section $\sigma_p = \pi\sqrt{2\alpha_p/E}$. The orbiting effect is expected to become important as $E \to 0$. This trend is apparent in the advanced adiabatic calculations, but not in the CTMC results.

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