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W.L. WIESE

Chairman of the Working Group

WORKING GROUP 3: COLLISION CROSS-SECTIONS AND LINE BROADENING

A. *Line Broadening*

Stark broadening (1) and polarisation shift effect in high density plasmas (2) have been reviewed. Critical reviews and a tabulation of selected data of the Stark widths and shifts of lines of non hydrogenic atoms and ions have been published (32,33).

1. Broadening and shift of spectral lines of hydrogen and hydrogenic ions in plasmas.

Interest in Stark broadening of hydrogenic lines arising from dense, high temperature plasmas (2) - (11) is increasing for several reasons; one of them is the possibility of doing an experimental study of the far wings: this has enabled to evince predicted satellite structure (10). At high and low densities, the increase of experiments concerning the study of the center of the lines and the neighbouring wings have given convergent results (9), (11), (12), (13), (19) concerning the disagreement with theory. The importance of ion dynamics seems now well established: earlier experiments showing the dependence of the central dip of H β on the reduced mass have been confirmed (12), (13). Yet the various theoretical attempts of calculation have all failed (14) - (16), with the exception of the MMM (model microfield method), which enables a uniform semi-classical unified treatment of electrons and ion perturbers (17), (25): strong effects are found in the line centers of Ly α , H α and H β which agree with earlier experiments but not with the most recent ones (20). Another Stark broadening mechanism has been suggested for taking into account the mass effect (3): The importance of the interference term is still being debated (21), (22) and fine structure effects have been pointed out (12), (23).

The theory of the line wings of hydrogen lines has made great progress, with particular attention paid to the Ly α , Ly β , H β asymmetry (24) - (31). A detailed quantum calculation of the electronic broadening with a "dissection" of the various contribution has been made (24) - (26): in the far wings of Ly α electrons are predominant, short range and quantum effects are important; exchange is of drastic importance as well as quenching effects (27): this leads to the conclusion that the Holtmark limit is a fiction. In the near wings ions become important and an improved semi-classical approximation including dipole, quadrupole and quadratic (polarization) interaction gives a correct asymmetry for Ly α but not for Ly β when compared to the experiment (31). For H β the asymmetry calculated with the dipolar exact resonance theory (28) is in agreement with (11).

2. Broadening and shift of non hydrogenic atoms and ions in plasmas.

For isolated lines, experimental results of the two past years (34) - (46) (Ca II, Na I, He I, N I, C I, Si II, Al I, Al II, alkaline earth, Si III, IV, Ne II, F II, Cl III, Ar II, U V) have confirmed the success of the semi-empirical and semi-classical impact perturbation theories. The unitarized quantum distorted wave calculation (45) agrees with the semi-classical one (39). This confirms the fact that the high order terms included in the determination of the perturber's trajectory are of minor importance (47). The MMM has been applied to isolated lines (48), (53) and agrees with earlier impact theories.

For conclusion, theoretical and experimental widths and shifts agree within 20-30% with a few exceptions. The remaining discrepancies are attributed to the inaccuracy of the atomic structure of the radiating atom introduced in the calculations of the collisional profile. Interaction of configuration and fine structure effects have been pointed out (49), (50), but their estimation is not always sufficient to remove the discrepancy (39), (45), (49).

A number of works concerning the overlapping lines of He has been done (52)-(54). As for hydrogen lines, mass effects have been found in the dip between the forbidden and permitted components of λ 4471, (51), (52), suggesting the effect of ion dynamics: in fact the MMM (53) gives a correct dip when compared to the experiments. The satellite structure studied in (54) has indicated that the interpretation in terms of Baranger-Mozer plasma satellites has to be excluded: He₂ molecular transitions are proposed.

3. Collision broadening by neutral atoms.

Tables of damping constants of spectral lines broadened by H and He have been prepared for the needs of astrophysics; calculations are based on a Smirnov-Roueff potential (55).

Apart from these works the actual preoccupations seem to move away from direct astrophysical needs. The impact broadening of the central regions of atomic lines perturbed by various rare gases and the related relaxation and depolarization cross sections have been studied in great detail, both theoretically and experimentally (56) - (66). Sophisticated semi-classical calculations (56) - (58) have shown the importance of rotational and fine structure inelastic coupling and have explained the different behaviour of the lines of a multiplet (62). However the most striking fact is the drastic importance of the interatomic potential at low and medium distances on the results; a great number of efforts are now directed towards this problem: ab initio theoretical potentials (67) and more recently model potentials have been provided (68), (69). Short range effects being more important far from the line center, the relationship between the potential and the intensities in the wings has received great theoretical and experimental attention (66), (70) - (72). Attempts have been made to carry on an unified adiabatic theory for permitted lines (71), (72). The nearest neighbour static limit has been used to determine semi-empirical interatomic potentials from the wings of resonance lines (66), (70). Since the recent discovery (73) of strong laser excited molecular emission from alkali noble gases systems (excimeres) associated with the far wings of quadrupole and two-photons forbidden lines, a new research area is now quickly developing (74) - (79): the electric dipole moment of the formed quasi-molecule is very sensitive to the internuclear distance since it vanishes at infinite separations; its calculation has been made for several systems (75), (76). This ensemble of theoretical and experimental research in line broadening and molecular structure is providing new tests for theoretical adiabatic interatomic potentials originating from various excited states; eventual applications to laser physics increases the interest for this new branch.

4. Interaction matter-radiation: line redistribution and polarization studies (Zeeman and Hanle effect).

Several theoretical studies have recently been completed concerning the redistribution of radiation reemitted by atoms in the presence of collisions (80) - (83). Experimental studies have also been performed (61) and departures from the impact regime of the redistribution function have been measured (84), (85). In the impact approximation, the angular distribution of the scattered radiation has been studied in detail (80). The first theoretical attempts to study the non impact regime have been treated in (81)-(83), but numerical calculations have not yet been performed though results of (81) are in qualitative agreement with experiments.

The quantum theory of optical pumping (Hanle effect) has been applied for calculating the linear polarization of helium lines in solar prominences and the first results in terms of magnetic field diagnostic have been published (86), (87). An article reviewing the various spectroscopic regimes ranging from the low field Zeeman effect to the high field Landau regime has been published (88): the relationship with solid state physics and with astrophysics, in the application to the study of magnetic white dwarf stars has been discussed.

S. SAHAL-BRECHOT

B. Collisional Cross Sections

Data centres: Nagoya University Japan collects and publishes data for fusion, in Japanese. English translation will follow (K. Tayanagi). Bibliographies are distributed by the International Atomic Energy Agency Vienna (ordered according to process: photon, electron, heavy particle cross sections) (89), by JILA (heavy particle cross sections including charge exchange, but not reactions) (90), and by Oak Ridge National Laboratory. A bibliography on molecular data including cross sections is distributed as Berkeley Newsletters, see Report of Working Group 5, ref (1). New Centres in Daresbury, UK, and in Berkeley, Cal. (NRCC = National Resource for Computing in Chemistry) have been established who will supply programs for the computation of cross sections. State of the art information may be gained by the book on the invited papers of ICPEAC X, Paris 1977 (91) which contains 47 talks on all aspects. Many details are found in the corresponding books of abstracts (92) of contributed papers, and in (93). A survey over many aspects of atomic collision processes was given at a meeting in honour of Sir Harrie Massey's 70th birthday (94), e.g. Photodetachment (Lineberger), dissociative attachment (Chantry), highly excited atoms (Stebbing), reactions (Bernstein), charge transfer (Hasted), fast heavy particle collisions (Bransden), inner shell ionization (Burhop), atomic excitation (Heddle), theory of electron molecule collisions (Burke), thermodynamic effects in recombination (Bates), and atomic physics from atmospheric and astrophysical studies (Dalgarno). Reports on atomic collision research in Japan (95) come out annually. Sil (96) reports on atomic collision research in India as represented at the Centenary Symposium of Indian Association for the Cultivation of Science (1976). Direct application to astrophysics is given by Dalgarno and Black (97) and by van Regemorter et al. (98) on molecule formation and destruction in the interstellar medium where many processes are discussed. Diffuse clouds are treated in (99). The ratio of deuterated to normal molecules in different situations is discussed in (100). Unstructured charged particles (electrons, protons, α -particles) are dealt with in (101) where a simple formula for optically allowed transitions is given, and in (102) which calculates orbital angular momentum transitions in highly excited hydrogen.

1. Heavy Particle Collisions

Because of the size of the field this report is restricted to general information, review articles and some literature as it came to the authors' notion. Many references had to be dropped. The reader will find them in the quoted literature.

Books: Two volumes on the dynamics of molecular collisions, edited by Miller (103), contain 13 articles, mainly on the theory of molecular collisions (Lester, Rabitz, Micha, Shin, Wolken, Siebrand, Porter and Raff, Kuntz, Hase, Child, Tully, Pechukas, Levine and Bernstein). In 1979 a book edited by Bernstein (104) on "Atom-Molecule Collision Theory: A Guide for the Experimentalist" will come out with articles by Child, Diestler, Kuntz, Levine and Kinsey, Light, H.F. Schaefer, Truhlar and Dixon, Truhlar and Muckerman, and Wyatt.

Reviews: Faubel and Toennies (105) deal with low energy vibrational-rotational excitation. A thorough review of the physics and mathematics employed by semi-

classical methods is given by Child (106) with many examples. Clark and Dickinson (107) use the Correspondence Principle to compare different approximations including the Strong Coupling Correspondence Principle approximation. De Pristo and Rabitz (108) stress especially the question of future lines of research as e.g. the "sensitivity" of "inversion" which means the reliability of extracting detailed molecular quantities from bulk properties. Truhlar and Wyatt (109) review H + H₂ energy surface and scattering. Many experiments have been done with laser excited atoms, especially Na(3²P^o), cf. Hertel and Stoll (110), who give a thorough theoretical introduction, and Hertel (111). Reactions and quenching of excited state atoms is described by King and Setser (112). Experiments of energy transfer of atomic excitation (Hg, alkali) to vibrations of the colliding molecule (H₂, O₂, N₂, etc.) are quoted by Lemont and Flynn (113). Highly excited "Rydberg" atoms ("free electron approximation", increase of lifetime by l-mixing) are dealt with by Edelstein and Gallagher (114) and by Takayanagi (115). Ion molecule reactions at thermal energies up to a few eV are reviewed by Ferguson (116) where many systems are quoted. A simple way of estimating charge exchange efficiencies at thermal energies on the basis of Landau-Zener approximation is mentioned by Dalgarno and Butler (117). Gayet (118) gives theory and rates for electron capture by protons at higher energies (25 - 200 keV). Different approximations for high (~10 keV) and low (~0.1 keV) energy are described and results compared with measurements by Basu et al. (119). Bobashev (120) considers quasi-molecular interference effects in ion-atom collisions and their effect on the polarization of emitted light. The excitation of inner shells in slow atomic collisions ($v < v_{\text{electron}}$, 1 - 100 keV) is discussed by Briggs (121). Reactive rearrangement collisions are mainly treated by statistical methods and chemical models, cf. Bernstein (94). Goldanski (122) shows that at very low temperature ($\lesssim 20$ K) activation energies of molecular reactions may go down, polymerisation may happen. Klein (123) describes isotope effects (mainly H-D) in chemical reaction rates quoting ratios of reaction or quenching rates. Bauer (124) gives a theory of chemical reactions including multiple scattering. Drift tube experiments of ion-molecule reactions at thermal energies (0.01 - 1 eV) are reviewed by Biondi (125).

In many papers the importance of the energy hypersurface describing the collision system has been stressed. Refined programs for ab initio calculations exist (126), (127). Electron cloud models together with asymptotic terms for large distances are suggested in (128), (129). A "Diatomics in molecules" model is used for H₂⁺(D₂⁺) + H₂(D₂) (130). Adjusted to measurements is the model (131). With sufficient theoretical background potentials may be extracted from scattering experiments for the spherically symmetric part of H₂-H₂, H-rare gas, H₂-rare gas cf. (132), (133). The stability of negative ions of polar molecules is discussed in (134).

Full close coupling quantum mechanical calculations for rotational excitation have been done for H₂-H₂ (135). For heavier systems the restriction to one input channel may allow an increase in the number of channels (136). Otherwise the number of coupled channels has to be reduced by some approximation. A few examples are given which guide to further literature. The "Coupled States" method (diagonalizing the body fixed centrifugal term) has been used to study He - HCN, Ar - N₂, Ar - HCl, H⁺- H₂ (137,138), He - HCl (139). A similar method ("decoupled l-dominant" method), suited for strong long range forces, has been applied to Ar - N₂, Li⁺- H₂ (140). A generalization is given in (141). A method suggested by Tang is applied to Ar - N₂, H⁺- H₂ (142). Sudden approximations are used to study the influence of the anisotropic part of the potential (143,144). Further systems (e.g. H₂-CS, H₂-OCS, He-HCN, He - N₂H⁺) are studied (145,146). Higher energies (a few eV), including vibrational excitation are considered for Li⁺-H₂ (147), for He-O₂, He-H₂ (148), for H₂-H₂ (149), and for H₂-He (150). Classical path calculations have been done for Li⁺- CO (126), for He - NH₃ (151), and for CO₂- He, Ar (152). K - NH₃ has been observed (153) and vibrational excitation of many atmospheric gases by H⁺, impacting on CO, CO₂ (154) and by Li⁺ on CO₂, N₂O (155), on H₂, D₂, N₂, O₂, CO, CO₂ (156). NO⁺ vibration is

efficiently quenched by N_2 (157,158), CO by aromatic hydrocarbons (159) and by O (160). Special attention has been paid to the system $H^+ - H_2$ experimentally (161) and theoretically (162). The cooling of hot interstellar gas by H_2 is discussed in (163). "Surprisal" analysis is used to generalize calculated results for special rotational transitions to others (164). Fine structure transitions are important for the cooling of interstellar clouds and for lasers. The following systems have been calculated: $H-C^+$, H_2-C^+ (165), $H-C$, $H-O$ (166), $F-H_2$ (167). $I - H_2O$ (168) was measured. For classical path calculations involving a change of the energy surface complex trajectories through the complex crossing point of the surfaces might be useful (169). Fine structure transitions in excited alkalis are measured for $Na 4^2D - \text{rare gas}$ (170). Deexcitation of alkali 2^2P states by N_2 , H_2 , O_2 is calculated in (171) and measured in (172). Elastic scattering of metastable $He 2^1S$ on rare gases has been measured (173), also ionization of rare gases by $He 2^1S$, 2^3S (174). Ionization of Ar by $He 2^2P$ is calculated in (175). The deexcitation of metastable highly charged hydrogenic ions ($Mg XII$, $P XV$, 2^2S) has been calculated (176). In collisions with highly excited "Rydberg" atoms the outermost electron may be treated as free (177). Ionizing collisions between Rydberg atoms are calculated in (178), and between a Rydberg atom and a polar molecule in (179). Electronic deexcitation of molecular $N_2 A^3\Sigma_u^+$ by N_2 , Ar, H_2 is reported in (180). A formalism to treat such cases theoretically is given in (181). Ionization of H_2 molecules by H_2 , N_2 at 0.2 to 5 keV was measured (182).

Many measurements and calculations refer to ion-atom, ion-molecule collisions. Rate constants between an ion and a polar molecule may be estimated by the "average dipole orientation" theory (ADO) which is improved in (183) for proton transfer reactions. For very low energies (< 1 eV) charge exchange cross sections may have a minimum, e.g. for Ne^+ , $Ar^+ - Ar$, Kr (184), cf. also $H^+ - D$ at 1 to 30 meV (185). For higher energies (< 200 eV) charge exchange cross sections for H^+ and rare gas ions in neutral rare gases are given in (186). A prescription how to correlate diabatic states of the electron exchanging system between small and large distances of the particles is given in (187). Charge exchange measurements with molecules are described for $Ar^+ - O_2$ at low energies (~ 1 eV) (188), and for C^+ , N^+ , $O^+ - N_2$ at 700 eV (189). An improvement on molecular theory for ion atom collisions is given in (190). Of great interest are charge exchange collisions with highly ionized species as calculated for $O^{+8} - H$ at 0.025 to 200 keV (191), and for H -like $- H$ at 4 to 200 keV (192). A theoretical discussion is given in (193) for e.g. HeH^{++} up to 50 keV. At high energies the electron may also be captured into a free state (194). Electron detachment from H^- in collisions with H , He have been calculated for energies of 10 keV to 10 MeV (195). Ionization of hydrogen by protons is calculated in (196) at 25 keV and 200 keV. Ionization of He by Li^+ at 2 to 5 keV was measured (197). Charge exchange may be accomplished by a radiative transition. Calculations have been done for $H - C^{++}$, C^{+++} , N^{++} at energies up to 10 eV (198). A semiclassical theory of radiative excitation transfer is given in (199). Radiative association of $C^+ - H$ has been calculated for temperatures of 20 to 1000 K in (200). Three dimensional calculations of the $H - H_2$ reactive system are reported (142,201). The following reactions have been measured: $HCO - NO$, O_2 , thermal (202), $O^+ - N_2$, O_2 , 300 to 900 K (203), $CN - NO$ (also in excited vibrational states) (204), O_2^+ , NO^+ , $O^+ - CO_2$, N_2 , CO , H_2 , Ar, NO , O_2 , thermal (205), $H_2CO - Ar^*(4^3P) \rightarrow CH^*A^2\Delta + \dots$, thermal (206), $N-NO$, 200 to 400 K (207), $O-I_2$, CS_2 , OCS , 50 to 300 meV (208). A statistical theory of ion-molecule reactions is given in (209). The spontaneous dissociation of H_2CO from excited levels is calculated in (211) and of H_2CO^+ in (210). For some molecules which can't be directly observed by radio astronomy protonated ions may be important (212). The proton affinity has been measured for CS in (213).

E. TREFFTZ

2. Electron collisions with, and photoionization of, molecules.

New results of general interest are being produced by the technique of laser

photoelectron spectrometry (214) - (217). Experimental low-energy electron scattering results have been reported, including rotational and vibrational excitation, and for some strongly polar molecules (218) - (221). A small number of low-energy cross-section calculations have been reported, including LiF, H₂, F₂ and CO₂ (222) - (225). Further results should soon be available from R-matrix calculations (226). There are calculations of dissociative excitation for H₂ (227) and H₂O (228) - (230). Photoionization calculations have been reported for H₂ and N₂ (231) - (234).

3. Electron collisions with, and photoionization of, atoms and ions.

A bibliography for electron - positive ion collisions (1940 to 1977) is found in (235). Useful reviews include: physical processes in planetary nebulae (236); atomic processes in hot plasmas (237); empirical formulae for excitation and ionization (238), (239); dielectronic recombination (240), dielectronic satellite lines (241); experimental ionization results (242), (243); ionization experiments and theory near threshold (244), (245); excitation of C and O ions (246).

The potentials to be used in collision calculations have been considered (247) - (251). Resonance contributions to excitation cross-sections have been considered (252). The Bethe approximation has been reviewed and generalised (253), (254). The importance of inner - shell contributions to ionization cross-sections has been stressed (244), (255), (256). A method of analytic evaluation of Coulomb Born integrals avoiding partial wave analysis has been given (257), (258). The accuracy of close-coupling and distorted wave calculations for special test cases has been assessed (259) - (263). Details of one of the standard close-coupling programmes have been published (264). The variable phase method of solving the close-coupling equations has been discussed (265). Experimental measurements of excitation cross-sections include: the resonance lines of K, Rb, Cs (together with polarization measurements and data on H, Li and Na) (266); 2s - 2p in C³⁺ (267); 2³P emission cross-section for Li⁺ (268); resonance lines of Sr, Ba and of Sr⁺, Ba⁺ (by electron impact with the neutral species) (269), (270). Close-coupling calculations have been reported for excitation of: C⁺ (2P_{1/2} - 2P_{3/2}) (271); C²⁺ (272); C³⁺ (273), (274); N⁴⁺ (275); O⁺ (forbidden) (276); O⁴⁺ (272); Ne⁷⁺ (277); Ar¹⁵⁺ (274); K (278); S⁺ (forbidden) (276). Distorted wave calculations have been carried out for excitation of atoms and ions too numerous to detail, see (279) - (289) and references therein. Similarly, for Coulomb-Born calculations, see (290) - (295).

Experimental ionization cross-sections have been measured for C³⁺ and N⁴⁺ (296); some results have also been inferred from plasma observations (297) - (299). Ionization cross-sections for highly charged ions have been calculated in the Coulomb Born approximation (300), and autoionization rates (and fluorescence yields) have been calculated for Li-like ions (301). Experimental measurements of dielectronic recombination in Fe⁸⁺ to Fe¹⁰⁺ have been reported (302). Calculations including the effect of autoionization with excitation have been made (303), (304). Results for He-like ions have been given (305), (306). The effects of microfields and collisions have been considered (307), (308). Several calculations of ionization balance and level populations in plasmas contain useful results on collision cross-sections and other atomic data, see (309) - (318). Photoionization measurements for O, Al, Fe and Ba (319) - (322), and calculated results for H⁻, C, N, O, F⁻, Ne (323) - (328) and a range of positive ions (329), (330) have been reported. Semi-empirical results for He are in (239).

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A. BURGESS

Chairman of the Working Group

WORKING GROUP 4: STRUCTURE OF ATOMIC SPECTRA

A. *Compilation and Bibliographies on Energy Levels, Wavelengths, and Line Classifications*

The ongoing program of the Atomic Energy Levels Data Center (National Bureau of Standards) to produce new compilations of critically evaluated energy level data is at present focused on the first thirty elements. The most recently completed compilations in this series give energy levels for all the spectra of Mn (Mn I-XXV) (1), Cr (Cr I-XXIV) (2), V (V I-XXIII) (3), Ti (Ti I-XXII) (4), Ca (Ca I-XX) (5), and Al (Al I-XVIII) (6), and work is underway on the spectra of K and Mg. C.E. Moore's "Selected Tables of Atomic Spectra" now include O I (7), O VI, O VII, and O VIII (8), work on the tables for the remaining oxygen spectra is in progress. A finding list for lines of the multiplets in Sections 1-7 of Moore's NSRDS-NBS 3 series has been compiled by Adelman et al. (9). A recent publication of the AEL Data Center, "Atomic Energy Levels - The Rare-Earth Elements" (10), gives energy-level data for 66 spectra of the 15 elements La through Lu ($Z=57-71$), including a number of astronomically important spectra. A review of rare-earth spectral data by Blaise et al. (11) gives partial tables of energy levels and wavelengths and includes data on hyperfine-structure and isotope shifts. The first version of a much needed new compilation of "Line Spectra of the Elements" has recently been published (12). These tables contain some 42,000 lines, including the stronger lines of the first and second spectra of 98 elements and lines of the third, fourth, and fifth spectra for about half the elements from the vacuum ultraviolet to the far infrared. Outred (13) has compiled 8885 selected lines of 57 elements in the infrared region 1-4 μm , with energy-level classifications being given where available. Energy-level and Grotrian diagrams for the atoms and positive ions of the elements H through P ($Z=1-15$) have been prepared by Bashkin and Stoner (14), and further publications for the heavier elements are planned. The AEL Data Center (NBS) expects to publish in 1979 a "Bibliography on Atomic Energy Levels and Spectra" for the period July 1975 through December 1978 (15). Edlén's 1976 review of term analysis of atomic spectra has references for spectra of the elements He through Ni (16), and Adelman et al. (17) have compiled an astronomically oriented bibliography on atomic autoionization. A bibliography on experimental isotope shifts in atomic spectra by Heilig (18) gives 666 references.

B. *Laboratory Research*

Reports on the research programs of a number of laboratories have been received. The present report is highly selective and incomplete regarding references to research on particular spectra, since the forthcoming bibliography (15) fully covers such references and will be widely available to astronomers.

I. Selected References, $Z \leq 28$

The references in Table 1 (in parentheses following the spectra) are a partial list of recent results for the elements through Ni. Several additional references for extensive isoelectronic-sequence results and a few references for spectra of heavier elements are given below.

II. Isoelectronic Sequences

Erickson (19) has calculated accurate energy levels for the one-electron species