

14. FUNDAMENTAL SPECTROSCOPIC DATA (DONNÉES SPECTROSCOPIQUES FONDAMENTALES)

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GENERAL

There is a continuing need for new and for improved data on wavelengths, atomic and molecular energy levels, transition probabilities and cross-sections, line broadening, and other parameters. The needs have been characterized by wider wavelength regions of interest, by the observation of more highly ionized species, by the growth of requirements concerning polyatomic molecules particularly in connection with interstellar matter, and by the steady increase in the demanded accuracy of the data.

Attention is drawn to the journals *Atomic Data and Nuclear Data Tables* and *Journal of Physical and Chemical Reference Data*, which do not seem to be well-known among astronomers. The latter journal in particular is publishing many compilations of data of interest to astronomers; some of these compilations are mentioned below. Among review articles covering several topics we mention Bashkin (1) and Martinson (2) on beam-foil spectroscopy. Garstang (3) gave a widely ranging survey of several areas of laboratory astrophysics. Walther (4) reviewed dye laser spectroscopy and Gabriel (5) highly charged ions in astrophysics.

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COMMITTEE 1: STANDARDS OF WAVELENGTH

A. *The Primary Standard and the Velocity of Light*

At present the primary standard of wavelength (and of length) is the ^{86}Kr line on which is based the definition of the International Metre (1) and the Ångström unit (10^{-10} m) (2). However a number of laser lines stabilized on molecular transitions in the visible and infrared by the use of Doppler-free spectroscopic techniques are much more precise. They have been measured against the ^{86}Kr standard with an accuracy limited by the uncertainty of the latter ($\sim 3 \times 10^{-9}$) and these measurements are more accurate than any others in terms of the metre. Furthermore, extension of the use of frequency comparison techniques to the infrared region has yielded the interrelation of the frequencies of these lines to others covering the range to the microwave part of the spectrum with an accuracy of 10^9 and better. This work already in 1973 had yielded sufficient accuracy and confidence in a knowledge of the velocity of light to lead both the BIPM (3) and the IAU (4) to recommend a value of $c = 299\,792\,458 \text{ m s}^{-1}$, with the

further recommendation that any new definition of the metre or second should, if possible, be made so as not to change this value.

Since 1973 a great deal of work has been done and is in progress on the use of frequency methods and on frequency measurements in the optical region of the spectrum as well as on improved laser stabilization, as reported in recent conferences in Paris (5), Novosibirsk (6) and Megève (7). The value of c adopted in 1973 has been confirmed by an independent measurement at NPL (8) and it appears extremely unlikely that any reason to change that value will result from other measurements in progress. Although there does not exist any continuously operating frequency locked system connecting optical region standards to the microwave region, there appears little doubt that such systems soon will be operational. Developments reported in the recent conferences cited suggest that the use of dye lasers, colour centre lasers, parametric oscillators, spin-flip Raman lasers, etc., will provide continuously tunable coherent sources for interpolating between frequency standards up to or through the visible, whose frequencies will be accurately known through the use of heterodyning and harmonic generation in high speed diodes, Josephson junctions, non-linear crystals, etc. It thus appears that it will soon be practical to define the metre and the second by means of a single electromagnetic source and the exact value of c given above, adopted by convention. Wavelengths from thermal sources would then be determined by reference to frequency standards whose wavelengths were derived by dividing their measured frequencies into the adopted value of c .

Although the Cs standard for frequency at 9.2 GHz is the most precisely established source at the present time, some of the absorption lines used in stabilized laser systems provide narrower lines and higher stability. For example, the 3.39 μm absorption line in methane has been observed (9) with a relative width of 10^{-10} , and a He-Ne laser stabilized to this line has a reported (10) stability of 10^{-15} . Although CH_4 has disadvantages of imperfectly resolved hyperfine structure and high proportional photon recoil and transverse Doppler effects, lines of heavier molecules such as CO_2 , SF_6 and OsO_4 (all at $\sim 10 \mu\text{m}$) show promise of at least as great sharpness but without many of the disadvantages of CH_4 . Well-studied laser systems stabilized by saturated absorption exist at 0.63 μm (He-Ne laser, I_2 absorber), 3.39 μm (He-Ne laser, CH_4 absorber), and 10 μm (CO_2 laser, several absorbers including CO_2) and others will undoubtedly appear in the near future. In addition, the technique of two-photon absorption may provide another Doppler-free method of relating laser frequencies to molecular absorption standards. At present it is not clear which of these sources or techniques will be the best and before such sources will present a serious rival in accuracy to the Cs standard a great deal of work is required to determine the magnitude of perturbations such as those due to pressure, electric and magnetic fields, and the servo locking system, as well as the more fundamental transverse Doppler and photon recoil effects.

The situation outlined in the first paragraph satisfies present requirements for the primary standard and it is to be hoped that the introduction of a new formal definition can await the completion of this new work. On the other hand there appears little point in further studies on characteristics of the ^{86}Kr standard which, having provided an excellent basis for the International Metre (through the use of a standard source rather than as originally defined), now has been linked with sufficient accuracy to the more precise He-Ne laser stabilized on lines I_2 or CH_4 with which other coherent sources can be more conveniently compared.

B. Secondary Standards

Reflecting the developments discussed above, a number of precise radiations suitable for standards in the infrared have been measured, and sometimes reported, as frequencies which are convertible to wavelengths through the recommended value of c . The most important of these are the CO_2 bands at 9 μm and 10 μm which are well known through wavelength measurements at NRC (11) and NPL (12) and frequency measurements at NBS (13) and NPL (14). The differences in frequencies of individual lines are very accurately known and can be used as standards in the THz region by the generation of difference frequencies in suitable detectors. Thirty-three P- and R-branch lines of the N_2O , 00^o1–10^o0 laser band have been measured to about $\pm 10^{-9}$ at NRC by reference to the CO_2 laser lines (15), and lines of a number of

CO transitions at $5\ \mu\text{m}$ have been measured, also by reference to CO_2 , to about $\pm 10^{-7}$ by Eng *et al.* (16) and confirmed at NRC. The following measurements related to wavelength standards were made following more traditional methods. Crosswhite (17) has published a list of over 4000 wavelengths between $1900\ \text{\AA}$ and $9000\ \text{\AA}$ for Fe I, Fe II, Ne I and Ne II produced in a hollow cathode discharge and has given data on intensity and some Ritz standards. Giacchetti and others (18) have used observations made by Connes' method of Fourier transform spectroscopy to produce a list of 3100 classified lines of Th I and Th II in the region between $0.9\ \mu\text{m}$ and $3\ \mu\text{m}$. The average deviation between observed and calculated wave numbers was found to be less than $0.002\ \text{cm}^{-1}$. Kaufman and Edlén (19) have published a compilation of reference wavelengths from Atomic Spectra in the range $15\ \text{\AA}$ to $25\ 000\ \text{\AA}$. Humphreys (20) has given descriptions of the first spectra of Ne, Ar and Xe 136 in the $1.2\ \mu\text{m}$ to $4.0\ \mu\text{m}$ region. An analysis of interferometrically measured wavelengths by the use of the Ritz principle and statistical methods and their application as secondary wavelength standards has been submitted for publication in the Journal of the Optical Society of America by Valero. Minnhagen has published two papers (21) and (22) on the spectrum of Ar I and Ar II and, with Kaufman (23) on ground term combinations in Ne I. Freeman at NPL is working on vacuum uv lines and has found several hollow cathode Ge II lines at $160\ \text{nm}$ to be very narrow and stable to better than $3\ \text{fm}$. Preliminary interferometric measurements on Xe I at $147\ \text{nm}$ are to appear in Optics Communications, and inert gas resonance sources are being studied. Vacuum uv work is also in progress by an NBS group on Y V to yield Ritz wavelengths in the region $200\text{--}470\ \text{\AA}$, and with Shenstone (24) to give accurate reference wavelengths of Cu III in the $380\text{--}850\ \text{\AA}$ and $1400\text{--}1700\ \text{\AA}$ regions. A new determination of the Rydberg constant was reported by Hänsch (25): his result is $109\ 737.314\ 3\ \text{cm}^{-1}$ with a standard deviation of 4 parts in 10^9 .

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COMMITTEE 2: TRANSITION PROBABILITIES

W. L. Wiese and his staff, operating the Data Center on Atomic Transition Probabilities, National Bureau of Standards, Washington, D.C., continue to collect all numerical results, and they can supply information as to what is available for any particular atom. They have published (1) a second supplement to their bibliography on atomic transition probabilities. They continue to make compilations of data. A compilation on forbidden lines of iron group elements has appeared (2), and a compilation (3) on allowed lines of Sc and Ti in all stages of ionization. Further compilations are in progress for V, Cr and Mn. The NBS staff have extended their investigations on oscillator strength regularities in iso-electronic sequences and have published several papers in this area. Calculated wavelengths and transition probabilities for many lines in the infrared spectra of many light elements from Li I to Ca II were given by Biemont and Grevesse (4). Weiss (5) reviewed configuration interaction effects. A new edition of the NBS tables of spectral-line intensities has appeared (6). Kurucz and Peytremann (7) have calculated or compiled over 265 000 oscillator strengths in the range 50–10 000 Å for many elements in their first stages of ionization, all intended for use in line blanketing studies. The Proceedings (8) of the Tucson beam-foil conference contains many papers and reviews on transition probabilities. In the following we can mention only a few of the many investigations which have been published or are underway. We omit references which may be found in *Astronomy and Astrophysics Abstracts*.

On the experimental side lifetimes by beam-foil spectroscopy have continued to appear, particularly from groups in Aarhus, Lyon, Stockholm, and Tucson. Some of this work has been directed towards spectral regions for which little data was previously available, for example measurements on C III–V in the far ultraviolet by Buchet-Poulizac and Buchet. Other investigators have worked on highly ionized atoms, an example being Cocke *et al.* (9) on S XIV–XV, and other atoms studied include O VIII, F IX, Cl XV and Cl XVI. Work has continued on many elements of astrophysical interest. Martinson, Curtis, Brzozowski and Buchta have measured lifetimes in Mn I and Mn II, Irwin and Livingston (10) in Si II–IV, Lundin, Engman, Hilke and Martinson in Mg I–IV, Irwin *et al.* (11) in Ne I–VI, Kernahan *et al.* (12) in N I–V, Lennard, Whaling, Scalo and Testerman in Ni I, Pinnington and Lutz in Mn I–III, Pinnington *et al.* (13) in O I–VI, and Biemont, Dumont and Grevesse in N I–IV. Interpretation of lifetime measurements requires knowledge of branching ratios, which have been measured by several authors, including Smith and Whaling, who used a hollow cathode discharge in work on Fe II, and Lennard, Whaling, Scalo and Testerman, who worked on Ni I. A notable development is the extension of lifetime measurements to many heavy elements. Andersen and Sørensen have published results on Pr II, Tm II, Lu II and Ce III, unpublished results are available for La II, Ce II, Pr II, Nd II, Sm II, Yb I, Yb II and Lu II, and work is in progress on levels of Hf, W, Th and Mo. Most of this work used beam-foil spectroscopy, and the Hanle effect was used in a few cases. Of particular interest is the introduction of new methods (14, 15, 16) of determining lifetimes free from the effects of cascades from higher energy levels by laser excitation. Results have been obtained by Walther's group for Na I (17), Fe I (18) and Ni I. Similar work at Kiel by Marek has given data for Cr I and Mn I. Furcinitti, Wright and Balling (19) remeasured the Mg I 3P_1 state lifetime by a dye-laser experiment. In another type of lifetime experiment Wells and Zipf (20) measured the O I 5S_2 state. Work with stabilized arcs has continued. Special mention must be made of coordinated efforts on Fe I by Bridges and Kornblith, and by May, Richter and Wichelmann. Over 500 of the strongest lines and an additional 1000 weaker lines were measured. Roberts, Voigt and Czernichowski studied transitions in Ti I–III. Heise measured many oscillator strengths in Ni I and Ni II, as did Goly, Moity and Weniger. Work is in progress at Meudon by Weniger on Cr I and Cr II. At Brest Johannin-Gilles *et al.* (21) obtained many values for Ti I, and have unpublished results on Sn I. Klemt published results for Ti I and Garz for Si I.

Shock tubes have been used for several studies. Wolnik and Berthel measured 90 Ti I and 30 Ti II lines. Roig and Miller (22) measured many lines in Co I and Co II, while Miller *et al.* (23) measured transitions in C I, S I and S II. Gilbert, Sulzmann and Penner gave results for Fe I. Shock tubes have also been used in measurements of photoionization cross-sections. This

was done by Kohl and Parkinson for Al I. Palenius, Kohl and Parkinson measured the cross-section for hydrogen, with results in agreement with theory. Work is now underway to make similar measurements on O I, and work on C I and N I is planned. The atomic beam method was used by Bell, Kalman and Tubbs for resonance lines of Ti I and by Mie and Richter for V I. Furnace absorption work has continued at Oxford, results being published by Blackwell, Ibbetson and Petford for Fe I and by Smith and O'Neill for Ca I, with additional work planned on the iron group elements. At Meudon work has been completed by Pujol and Weniger on many transitions in Mn I. The Hanle effect has been used by many authors, including Hilborn and de Zafra for Fe I and Becker, Göbel and Klotz for Ni I. The method of delayed coincidence was used by Burshtein *et al.* (24) in work on Yb I and Yb II. The book method continues to be used. Banfield and Huber measured ultraviolet lines of Fe I and Fe II. Huber *et al.* (25) studied Cr I lines below 2000 Å and work is in progress at longer wavelengths. Work is also underway on 250 lines of Ni I. Mitchell (26) studied the principal series and intercombination lines in Mg I. Smith is working on Ti I; he is also determining corrections to the *gf*-value data of Warner for the second spectra of the iron group, and evaluating the results of Kurucz and Peytremann mentioned earlier. Penkin and Komarovskii (27) published results for Gd I, Eu I and Nd I, and with Smirnov (28) for Dy I. Parkinson, Reeves and Tomkins have completed measurements on many members of the principal series of Ca I, Sr I and Ba I, and on a number of two-electron jumps in these ions. They are also working on Sc I.

Weisheit and Shore investigated the effects of plasma screening on oscillator strengths and photoionization. They showed that such effects cause high series lines to fade away, rather than merge. This will modify the usual interpretation of series termination with the aid of the Inglis-Teller formula.

Theoretical studies have given emphasis to configuration interaction effects. Trefftz *et al.* have studied the interplay between spin-orbit interaction and configuration interaction (29), made applications to Ba I (30), and have recently completed work on Si X. The relationship between the dipole length and dipole velocity forms of transition integrals was investigated by Trefftz. Hibbert (31) made studies of the Be I sequence. Transitions of the form $s^a p^b - s^{a-1} p^{b+1}$ have been studied by various authors, these transitions require moderately refined calculations if accurate oscillator strengths are to be obtained. Sinanoglu, Beck and Nicolaidis (32, 33, 34) have performed calculations on such transitions in various first and second row atoms, and further work on Li I, N I and N II has recently been finished. Van Rensbergen, Sakhibullin and van der Hucht have worked on two-electron jumps in C II. Nussbaumer has studied many atoms using configuration interaction techniques, including Fe XIII and the Be I isoelectronic sequence; work has been completed but not yet published for the Na I sequence and for O IV (with D. R. Flower), Fe X, Ni XII, and (with M. Loulergue) Fe XVII and Ni XIX. Malinovsky has completed work on O V. Other theoretical investigations have included charge expansion calculations by Laughlin and Dalgarno (35, 36) on transitions of the form $s^a p^b - s^{a-1} p^{b+1}$ in several isoelectronic sequences, and Laughlin, Lewis and Horak on the Li I and Na I sequences. Calculations of $^1S_0 - ^3P_1$ intercombination lines have been made by Laughlin and Victor for Be I and Mg I, and by Kononov *et al.* (37) for the Be I isoelectronic sequence. Biemont has studied trends of Hartree-Fock oscillator strengths in the Na I and K I sequences. He has also made extensive use of the scaled Thomas-Fermi method. Cowan has continued his collaborations with Culham, NRL, and elsewhere, predicting energy levels, wavelengths and oscillator strengths for many lines in highly ionized atoms which occur in the solar spectrum and in laser-produced plasmas. His work covered many stages of ionized iron, ranging from Fe VI to Fe XXIV, and some transitions in manganese, chromium, vanadium, and other elements. In (38) lines of Fe IX–XVI and Mn VIII–XV were discussed, and several other papers were published by Cowan. In unpublished work Grineva, Safronova and Urnov have calculated radiative and autoionizing probabilities for many transitions in Fe XVIII–XXV. The effects of high (megagauss) magnetic fields on energy levels and line intensities have been calculated by Garstang and Kemic, and by O'Connell and colleagues, atoms studied being H, He I, He II and Ca II. Relativistic effects have been considered. They are small for light elements in low stages of ionization but may become important for highly ionized atoms. Younger and Weiss, in unpublished work, have considered hydrogen-like ions, and studies are in

progress on the Be and B sequences. Configuration interaction and intermediate coupling effects are also included in the calculations. Klimchitskaya, Safronova and Labzovskii have completed relativistic transition probability calculations in the He sequence for arbitrary Z .

Measurements (39) of forbidden line transition probabilities for O I and S I are of interest in confirming earlier theoretical results, and work has subsequently been completed on Se I. Important work has been done on the $2^3S_1 - 1^1S_0$ in helium-like ions, including its observation (40) in He I by Moos and Woodworth, theoretical calculations by Kelsey and Sucher (41), and measurements of lifetimes for the 2^3S_1 state in several ions including S XV, Cl XVI, Ar XVII and Ti XXI, many references may be found in (42). Laughlin (43) and Onello and Ford (44) have studied magnetic quadrupole transitions.

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R.H. GARSTANG
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COMMITTEE 3: COLLISION CROSS-SECTIONS AND LINE BROADENING

A. Line Broadening

Besides a comprehensive monograph on spectral line broadening by plasmas (1) two review articles have been published dealing with this subject in the more general frame of plasma spectroscopy (2, 3). Especially the broadening by neutral particles is the topic of the review articles (4, 5, 6). The bibliography on line broadening has been and is being continued (7).

I. Collision Broadening by Neutral Atoms

Line broadening by neutral particle impact is largely determined by chemical forces rather than van der Waals interactions, especially for light perturbers like H and He (8). For alkali-like lines perturbed by He a simple approximation to exchange repulsion was used which gives good agreement with experiment (9). The same approach is applied to the solar infrared multiplets of C I, O I, Si I in (10). A generalization allows the calculation of damping constants (11). For any given line and temperature the damping constant can be easily found from a set of tables. The above mentioned approximation is less suited for heavy perturbers (12) or attractive chemical forces. For the broadening of sodium D lines by hydrogen a numerically calculated molecular potential was employed together with rotation and fine structure effects (13). A theory which covers not only the impact regime of the line but also the quasistatic wings was developed (14). The transfer of excitation in resonance broadening is considered in (15), the influence of the Doppler effect on resonance broadening in (16). Ref. (17) points out that depolarization changes over the width of the line, the far wings being completely depolarized.

Different from the direct astrophysical interest in line shapes is the aim of experimental work on the extreme wings. By carefully studying temperature and pressure dependence of far wing emission alkali-noble gas interaction potentials could be constructed for lower and upper states of the transition in the range of a few Ångströms (18). In a much simpler way interaction potentials are determined by assuming them to be of Lennard-Jones form ($ar^{-6} + br^{-8} + cr^{-12}$) where the coefficients are extracted from experiment (19). For selfbroadening (resonance broadening) the asymptotic r^{-3} potential describes the shape of the line wings well (20). Schuller and Behmenburg (5) give a review on these methods.

Lineshapes of molecular rotational and rotation-vibrational transitions are reviewed by Rabitz (21).

II. Broadening and Shift of Spectral Lines of Non-hydrogenic Atoms and Ions in a Plasma

Critical reviews of the widths and shifts of isolated spectral lines emitted by non-hydrogenic atoms and ions are being published (22, 23).

In the case of the He I lines with forbidden components it is still an experimentally (24, 25) and theoretically (26) open question, whether at medium and low electron densities ($\leq 10^{15} \text{ cm}^{-3}$) the influence of ion dynamics, chiefly on the intensity maximum of the forbidden component, is so distinct as has been supposed (27) and had been predicted by former theories (28, 29, 30). The theory (30) has been the basis for tables of the profiles of He I $\lambda = 4471 \text{ \AA}$ (30) and $\lambda = 4922 \text{ \AA}$ (31) which have been applied to the profiles of these lines in B-stars (32, 33).

III. *Broadening and Shift of Spectral Lines of Hydrogenic Atoms and Ions in a Plasma*

The customary theories of broadening of hydrogenic lines describe the plasma ions as quasi-static and the plasma electrons according to impact or unified theories.

Problems of the quasistatic microfield distribution have been treated in (34, 35), the distribution of the average of the low-frequency component (ion produced) of the time-dependent microfield taken over a finite time interval has been studied in (36). The unified theory for electron broadening (37, 38) has been rederived (39) and methods of including time ordering to all orders in the collision operator (40) have been extended to hydrogenic ion lines (41, 42, 43). For reasons of computing time approximations to the collision operator (44) cannot be avoided in the case of lines with high upper main quantum numbers. Tables of the profiles of Lyman- and Balmer-lines of neutral hydrogen (45) are based on the unified theory (without taking account of time ordering to all orders). For the considerable differences between these tables and another set of tables, reprinted in (1) and based on the modified impact theory, compare (46, 47, 48, 49). As is well known, neither theory coincides with experiment near the centers of low Balmer lines at low and high electron densities. Regarding the unified theory (45) the discrepancies can be reduced by allowing for time-ordering (50). That the remaining discrepancies might be completely attributed to ion motion, seems to be proven by experiment (51). This effect, if real, cannot be explained by any one of the theories (52); for further references see (51). Taking into account the electric fields from ion sound waves ref. (53) reports a much improved agreement between the modified impact theory and experiment.

The theory of the line wings, especially of Ly- α , has been developed in great detail (54, 55, 56, 57), a serious discrepancy between theory and experiment has been cleared up (58). There seems to be some evidence (59) for an experimental identification of the satellites predicted in (55, 56).

The experimentally observed asymmetries and shifts have been studied theoretically (see (60) for further references).

B. *Collision Cross-Sections*

Since the last report activities in the field of collision cross-sections have grown further. Especially the needs of astrophysicists and the results of chemists are approaching each other rapidly. This report therefore cannot give full account of all present day work.

A survey of physical chemical data centres is given by Lide and Rossmassler (61). For the last two ICPEAC conferences abstracts were published (ordered according to type of collisions), and also invited papers (62–65). For given molecules references on collision data are quoted in *Berkeley Newsletters* (66).

The following general aspects of collision theory and approximations have been reviewed: 'Classical Limits of Quantum Mechanics and the Theory of Molecular Collisions' by Miller (67), 'Correspondence Identities and the Coulomb Potential' by Norcliffe (68), 'Impact Excitation and Polarization of the Emitted Light' by Fano and Macek (69), 'Recombination' by Bates (70), 'Detailed Balancing in the Time-Dependent Impact Parameter Method' by Gerjuoy (71), 'Applications of the Glauber Approximation to Atomic Collisions' by Gerjuoy and Thomas (72), 'Coupled Integral Equation Approach to Nonrelativistic Three-body System with Applications to Atomic Problems' by Chen (73), 'The First Born Approximation' by Bell and Kingston (74), 'Pseudopotentials in Atomic and Molecular Physics' by Bardsley (75). An account of experimental work on 'The Role of Metastable Particles in Collision Processes' by Rundel and Stebbings (76) describes chemi-ionization and other processes caused by excited atom impact. Activities in Japan are reported on by Takayanagi (77).

I. *Heavy Particle Collisions*

Ion-molecule reaction rate data are collected and a bibliography is published by Sinnott (78). 'Rate Constants of Thermal Energy, Binary Ion-Molecule Reactions of Aeronomic Interest'

has appeared (Ferguson, 79). A multiauthor book on *Ion-Molecule Reactions*, mainly from an experimentalist's point of view was edited by Franklin (80). Child (81) in his book on *Molecular Collision Theory* describes mainly semiclassical methods. The book of Nikitin on *Theory of Elementary Atomic and Molecular Processes* has been translated (82). Many articles of interest are contained in (83).

Reviews on vibrational and/or rotational transitions have been given by Secret (84) (theoretical methods), George and Ross (85) (quantum mechanical theory), Oka (86) (rotational transitions, theory and measurement), Ormonde (87) (vibrational relaxation, theory and measurement, mainly hydrogen halides) and Moore (88) (vibrational transitions, mainly experimental). Ionic recombination is reviewed by Mahan (89) (experiments) and by Moseley *et al.* (90) (experiments and calculations). Reviews on charge exchange are given by Taware and Russek (91) (measurements) and by Bransden (92) (theory). Rudd and Macek (93) review ionization by ion impact on atoms. The problem of reconstructing interatomic potentials from atom-atom (ion) scattering data is treated by Buck (94).

A most difficult problem is the description of chemical reactions. Reviews on experimental reaction rates are given by Dubrin (95) (up to about 10 eV), by Westenberg (96) (room temperature), and by Farrar and Lee (97), where further recent reviews are cited. Some theoretical work is reviewed in (81) and in (85). Monte Carlo calculations of classical trajectories are discussed and compared with other methods by Keck (98) and by Porter (99).

Fine structure transitions by heavy particle impact are described in (100) ($\text{Cs}(6^2P)+\text{Kr}$, $\text{Cs}(6^2P)+\text{CH}_4$, rotational enhancement), (101) ($\text{Li}(2^2P)+\text{He}$, $10^{-4}-10^{-2}$ eV), (102) ($\text{Na}(3^2P)+\text{He}$, 400–4500 K), (103) (C^++H_2 , 10–1000 K), and (104) (C^++H). Rotational excitation cross-sections have been calculated in close coupling approximations for Li^++H_2 (about 1 eV, including vibrational excitation) (105), for $\text{Ar}+\text{H}_2$, 1 to 4 meV (106), for $\text{H}+\text{H}_2$, 0.05–0.25 eV (107), for $\text{He}+\text{CO}$ up to 10 meV (108) and for $\text{He}+\text{HCN}$, 1.5–70 meV (109, 110). Further systems treated are $\text{He}+\text{H}_2$ (111, 112, 113), $\text{He}+\text{HD}$ (114), $\text{He}+\text{N}_2$ H^+ (115), $\text{He}+\text{HCl}$ (116), $\text{He}+\text{H}_2\text{CO}$ (117), $\text{H}+\text{CO}$ (118, 119), H_2+CO (120), H_2+HD (121), H^++CN , 40 meV–500 eV (122), and as an example for a heavy, strongly polarized molecule $\text{He}+\text{TlF}$ (123). For $\text{H}+\text{H}_2$ the angular distribution of elastic scattering and rotational excitation is calculated in (124). Measurements on vibrational deactivation of $\text{HF}+\text{H}$ are reported in (125). Approximations and general aspects of this kind of low-energy scattering are given in (126), (127) applied to $\text{He}+\text{H}_2$, in (128) applied to H_2+H_2 , and in (129). The different approximations are discussed in (130–133). The role of complex trajectories in semiclassical calculations of elastic scattering is discussed in (134).

(135) and (136) deal with interatomic potentials between noble gases, cf. also references in (135). A comparison of approximate potentials to *ab initio* calculations is given in (137) for $\text{He}+\text{H}_2\text{CO}$ and Li^++H_2 . In the system $\text{H}+\text{H}_2$ the anisotropic parts of the potential are still not well established (138). A new method for the calculation of intermolecular potentials is suggested in (139). Orbiting resonances which occur in weakly binding potentials have been measured (140) and calculated (141) for $\text{H}(\text{D})+\text{Hg}$ at about 3 meV. They were also found for $\text{H}+\text{Xe}$ between 1 and 2 meV (142).

The vast field of reaction cross-sections is more or less restricted to experimentally accessible regimes. Quantum mechanical 'model' calculations in this field are mostly one-dimensional. Three-dimensional quantum mechanical calculations have been done for $\text{D}+\text{H}_2 \rightarrow \text{HD}+\text{H}$ (143), cf. also the measurements (144, 145). A new semiclassical treatment is suggested in (146). General aspects are discussed in (147). Three-dimensional semiclassical trajectory calculations are reported in (148) for $\text{H}+\text{F}_2 \rightarrow \text{HF}+\text{F}$ and in (149) for $\text{H}+\text{Cl}_2$ and $\text{Cl}+\text{H}_2$. High reaction rates may be expected from impacts of excited atoms like $\text{A}+\text{B} \rightarrow \text{AB}^++\text{e}$ (150) or $\text{A}+\text{B} \rightarrow \text{A}^++\text{B}^-$ (151 and references therein). (152) refers to $\text{He}(2^3S)$ + rare gases. Many ion-atom, molecule reactions have been or are being measured by the group of Ferguson, Fehsenfeld, and coworkers, see e.g. (153, 154). Dissociation of H_2 by alkali ion impact at 5 to 50 eV has been measured and compared with a hard sphere trajectory calculation in (155). At similar energies electron capture by α -particles in noble gases has been measured in (156). Na^++K charge exchange was compared to resonant charge exchange K^++K for 0.1–2 eV in (157).

Oscillatory structure in resonant charge exchange of alkalis and noble gases is explained by

calculations in (158). Close coupling calculations for p+H charge exchange at keV energies have been done using Gaussian basis sets to describe the wave functions (159). The angular distribution of electrons produced in $\text{He}^+ + \text{He}$ collisions at 15 keV was measured (160). The astrophysical implications of multiply charged ion charge exchange in helium is considered in (161).

An approach which applies to all kinds of cross-section data is the information theoretical method advocated by Levine *et al.* (162). Actual populations of reaction product states are compared to statistical populations. The method allows to describe irregular populations by simple functions (e.g. 163) ('surprisal', entropy deficiency), and to use this information for the estimation of other quantities (164).

II. Electron Collisions with Molecules

In electron-molecule scattering experimental techniques are considerably ahead of their computational counterpart. A new technique of using He as a secondary standard for the determination of absolute cross sections has been developed by Srivastava *et al.* (165). There is much activity in Trajmar's group in the intermediate energy range (5–100 eV above threshold) using this technique. Itikawa (166) has reviewed the momentum transfer cross-sections available. Recent experimental papers are listed which indicate the current activity in elastic and momentum transfer cross-sections (165–169), rotational excitations (165), vibrational excitations (170–173), electronic excitations (174–183) and dissociation processes (184–194).

Activity in theoretical work is just starting. Low energy cross-sections (0–10 eV) are reviewed by Takayanagi (195). Schneider (196, 197) has been developing an extensive program aimed at including polarization and short range correlation effects accurately. Other recent papers on elastic cross-sections are listed (198–202). Chu and Dalgarno (203) and Chu (204) have developed the Coulomb-Born approximation for the rotational excitations of ions with permanent dipoles and applied it to the astrophysically important species CH^+ and H_3O^+ . Other recent papers deal with rotational excitations (205–207).

III. Electron Collisions with Atoms and Ions

A bibliography of all electron and photon cross-sections published before 1975 (edited by Kieffer and Beaty) is in press (208). A general review of electron impact excitation of positive ions at thermal energies is given by Seaton (209). Reviews of theoretical methods to describe e⁻-atom scattering at low energies are given by Nesbet (210), Burke and Robb (211), Geltman (212), Percival and Richards (213), Rudge (214) (excitation), and Byron (215) (eikonal methods), Joachain and Quigg (216) ('multiple scattering expansion'), McCurdy *et al.* (217) ('many body theory'). Relativistic effects in electron-atom scattering were treated by Jones (218). Momentum transfer cross-section data – both theoretical and experimental – were compiled by Itikawa (219).

Andrick (220) gave a review of experiments on differential elastic cross-sections, while the review of Schulz (221) describes especially resonances in electron impact on atoms and molecules.

Many articles were written about computational methods to calculate collision data (222, 223), cf. also the collection (224). Of special interest are recent investigations of electron scattering by laser excited atoms (225, 226).

In the following we quote only latest papers where further references may be found.

Besides the astrophysical need for reliable data two major aims are prosecuted: to describe the angular dependence of cross-sections correctly, and to bridge the energy gap where close coupling calculations become impractical while Born approximation does not yet hold.

Eikonal approximations are developed in (227) ($\text{He } 1^1S \rightarrow 2^1S$), in (228) (H elast, 20–100 eV), in (229) ($\text{He } 2^1,^3S \rightarrow 2^1,^3P$, $n = 3$ states, no exchange), in (230) (Li elast, 54–200 eV). They are used in (231) (Li^+ elast with optical potential), (232) ($\text{He}^+ 1s \rightarrow 2s, 2p$, $E = 40\text{--}300$ eV), (233) (H, $n = 1, 2, 3$ coupled, 20–200 eV). 'Many body theory' has been applied in 1st order and compared with measurements for $\text{He } 1^1S \rightarrow n = 3$ states (234). It was developed for ionization processes in (235). Good results have been achieved with distorted

wave polarized orbital methods for excitation of H, He⁺ (236, 237) and – less good – He (238). Optical potentials have been constructed and used in (239) (He, Ne elast., 400 eV), (240) (Ar elast. 500 eV). In (241) optical potential results are compared with distorted wave results for H 1s → 2s excitation, 10–50 eV.

There are 2 attempts (242, 243) to treat scattering on hydrogen as a 3-body problem.

Several computer programs for close coupling calculations have been developed and extensively used for astrophysically important transitions: (244) ([O III], [N II], [Ne II], [Ne III]), (245) (highly ionized forbidden transitions), (246) (N⁴⁺), (247) ([N II]), (248) ([O I]). (249) uses an algebraic close coupling method (H 1s → 2s, 2p, 10–20 eV). In (250) a close coupling model calculation is done for He around the threshold of 2³S. First relativistic close coupling calculations on Cs are reported in (251).

For highly ionized atoms intermediate coupling must be taken into account. Excitation cross sections for He-like Si XIII, Ca XIX and Fe XXV have been calculated in intermediate coupling distorted wave approximation (252). Elastic ‘scattering factors’ calculated from the Dirac equations are tabulated for neutral atoms for energies of 100 to 1500 eV (253). Their usefulness for smaller energies is tested in (254) (Li, 2–10 eV). Excitation cross-section data on O and N and their ions will be published in (255).

The construction of suitable potentials is discussed in (256) and (257), the effect of correlation in the target in (258, 259), and as well in the system e+target in (260). A simple generalization of the Born approximation is tested in (261, 262). Born approximation is used for Be excitation cross-sections in (263). A semiempirical formula for excitation and ionization is employed in (264, 265) for He and He-like ions. (266) uses dispersion relation together with the best available cross-sections to determine the elastic forward scattering amplitude for He and Ne from 3 to 1000 eV. Measurement of Xe ionization is suggested based on a Born approximation calculation with correlated target wave functions (267).

Most of the measurements refer to inert gases. Elastic differential cross-sections are given in (268, 269, 270) for He, in (271, 272, 273) for Ne and others, in (274) for H (20–680 eV). Differential cross sections for excitation are reported in (275, 276, 277) for He, (278) for Ar. For large scattering angles Born approximation gives wrong results even for high impact energies (275). Structure in cross-section (resonances) is studied in He (279) and in He, Ne, Ar (280). No resonance structure has been found in hydrogen between 0.5 and 9 eV (281). The differential cross-section for He 1¹S–2³S excitation is abnormally high in forward direction (282). Generalized oscillator strengths have been determined for He (283).

For many metals total excitation cross-sections have been measured via optical line emission: K⁺, Cs⁺ (284), Ba (285), Ga, Ga⁺ (286), Al (287). Rate coefficients for excitation and ionization of highly ionized iron, Fe VIII, Fe IX, Fe X were observed in a θ -pinch (288). For Pb differential elastic and inelastic cross-section at 40 eV impact energy were measured (289). Total ionization cross-sections for Al, Ga, In, Tl at impact energies of 50 to 500 eV are given in (290). Several papers describe ionization via autoionizing levels: He (291), K (292, 293). Also in Rb⁺, Cs⁺, Ca⁺, Sr⁺ ionization is influenced by autoionizing levels and/or inner shell ejection (294). For Kr angular correlations of the ejected electrons have been observed (295).

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ELEONORE TREFFTZ
Chairman of the Committee

COMMITTEE 4: STRUCTURE OF ATOMIC SPECTRA

Publication of a Bibliography on Atomic Energy Levels and Spectra (1) covering the period July 1971 through 1975 is expected during or before the summer 1976. Since papers on particular spectra are fully covered in this bibliography, this report will in general be confined to noting several reviews and compilations of laboratory data useful for astronomical spectroscopy and to a summary listing of some of the work now in progress. Work mainly of interest for data other than atomic energy levels and line classifications is not listed here.

A. *Compilations, Reviews*

Kelly and Palumbo (2) have published their critical tabulation of 34 700 lines with wavelengths from 1 Å to 2000 Å. It includes all observed spectra of the elements H through Kr published up to May 1972, and gives the term classifications. An extension of these tables to 3000 Å is in progress. A review of *Recent Progress in the Classification of the Spectra of Highly Ionized Atoms* by Fawcett (3) includes a bibliography keyed to the spectra. Fawcett also has compiled line lists of the $2s^2 2p^n - 2s2p^{n+1}$ and $2s2p^n - 2p^{n+1}$ transitions for the elements Li through Ni, and derived energy levels from the wavelengths (4). Outred (5) is maintaining a library of atomic lines in the infrared (1–4 μm) and plans to publish a compilation of such data. A *Bibliography of Atomic Line Identification Lists* to supplement the available compilations has been published by Adelman and Snijders (6). Section 5, N I to N III, of C. E. Moore's series of *Selected Tables of Atomic Spectra* (7) has appeared, and the manuscript for O I is complete. Multiplet tables and tables of energy levels are given for each spectrum in this series. Reader and Sugar (8) have compiled the energy levels of the iron atomic species, Fe I through Fe XXVI, and similar tables for chromium are being compiled at NBS by Sugar and Corliss. A new compilation of the energy levels of helium was published (9). A compilation of the energy levels of the rare earths (La through Lu, $Z = 57-71$) is at an advanced stage, and it is hoped that the tables for most of the more than 60 spectra will be in press by the summer of 1976 (Martin, Zalubas, Hagan, NBS). Pending completion of these tables, a compilation of the ionization potentials and ground-level designations for lanthanide and actinide atoms and ions was published, including a selected bibliography on analyses of the corresponding spectra (10). Blaise and Wyart (11) have reviewed work on the lanthanide spectra up through 1972. Bashkin and Stoner (12) have prepared new energy-level and Grotrian diagrams for the atoms and ions H I through P XV. A second volume of such diagrams will probably cover the elements S through Fe. Edlén's 1972 review of the term analysis of atomic spectra has been published (13). It concentrates mainly on the first 28 elements and includes an extensive bibliography complete to November 1972. Some compilations and data centers for atomic spectroscopic information were described in a 1974 review in somewhat more detail than is possible here (14).

B. *Work in Progress*

The numbers following the spectra listed in the table below indicate laboratories having experimental wavelengths and/or energy level data that were not published by June, 1975. The addresses of the laboratories are given in a separate numbered list. The person whose name is given after the laboratory address either supplied the information on the program of that laboratory or was suggested as being appropriate for this listing. Although this summary is certainly incomplete, it should nevertheless be helpful to astronomers as a guide to ongoing laboratory research. Although wavelength ranges are not listed, they may usually be roughly

inferred from the ionization stage. Probably most exceptional in this regard are the investigations of neutral spectra listed for the NBS Far Ultraviolet Physics Section (Laboratory 9) and for the Imperial College-Bonn-Physikalisches Institut Group (Laboratory 29); these mainly involve inner-shell absorption transitions at wavelengths below 1200 Å.

Table

Spectrum	Lab.	Spectrum	Lab.	Spectrum	Lab.
Li I	9	Ca I	29	Ge I	19
Be III	1	Ca X	3, 20	Ge V–VI	22
B I	14	Ca XIV–XVII	22	Se I	6
B III	27	Sc I	6	Br II	8
B IV	1, 7	Sc V	3	Kr I	29
B V	7	Sc XI	20	Kr II–IV	2
C V	1	Ti II, V–VII	3	Kr IV, V, VII	31
N III	2	Ti XII	20	Rb I	29
N V	27	Ti XX	19	Rb III	8
N VI	1	V I	21	Rb III, IV	2
O II	3	V II	4	Sr I	21
O III	2	V V	11	Sr IV, V	2
O V, VII	27	V VI	3	Y I	21
O VI	22, 27	V XIII	20	Y IV, V	8
Nc III	2	V XXI	19	Y VI	8, 33
Na IV	2	Cr III	3, 4	Zr IV–VI	8
Mg I	9	Cr VII, VIII	3	Zr VII	8, 33
Mg V	2	Cr XIV	20	Zr XII–XIV	8
Al I	14	Cr XXII	19	Nb V–VII	8
Al II	8	Mn VI	18, 28	Nb VIII	8, 33
Al V, VI	1	Mn VII	11	Nb XIII–XV	8
Al XII, XIII	32	Mn XV	20	Mo I	8
Si V	1	Fe I	3, 8, 14, 19	Mo VI–VIII	8
P I, II	3, 7	Fe II	3, 14	Mo IX	8, 33
P III	3	Fe IV	3	Mo XIV–XVI	8
P IV	3, 31	Fe VI	22	Mo XVI–XXI	30
P XII, XIII	24	Fe VII	3	Ru III	4
S II–VI	3	Fe XIX–XXII	22	Rh III	4
S XIII, XIV	24	Fe XXIII–XXV	30	Ag I	29
Cl IV–VII	3	Co II, III	4	Ag IV	5
Cl XIV, XV	24	Co IV, V, VI	5	Cd I	19, 29
Ar III, IV	2	Ni III	4	In I	29
Ar VII	31	Ni IV–VII	5	Sn I	19, 21
K I	29	Cu I	29	Te I	6
K II	2	Cu II	21		
K IX	3, 20	Cu III	8, 23		
		Cu IV–VI	5		
		Zn I	19, 29		
		Zn IV, V	25		
		Ga IV–VI	22, 25		

Spectrum	Lab.	Spectrum	Lab.	Spectrum	Lab.
Xe II-IV	2	Ho I	6, 29	Au XI, XII	8
Cs I	29	Ho II	6	Tl I	29
Cs II	8, 21	Ho III	10	Tl XIII, XIV	8
Cs III	8	Er I	5, 6, 29	Pb I	29
Ba I	14, 29	Er II	5, 6	Pb XIV, XV	8
Ba II	14	Tm I	29	Bi I	6
Ba III	2	Tm II	6, 8	Th I, II	8
Ba IV	8	Yb I	8, 29	Th IV	18, 26
La I	6, 29	Hf I	15	U I	6, 16, 17, 26
La IV, V	8	Hf V	8	U II	6, 16
Ce I	8	Ta III, IV, V	5	U IV	18, 26
Pr I	6, 8, 29	Ta XI-XIII	8	U V, VI	8, 16, 18, 26
Pr II	6, 8	W V, VI	5	U VII	8, 16
Nd I	29	W VII	8	Np I	6, 17
Nd III, IV	10	W XII-XIV	8	Np II	17
Pm I, II	8, 11	Re II	4	Pu I, II	6, 17
Sm I	29	Re VII	5, 8	Am I, II	17
Eu I	12, 29	Re VIII	8	Cm I	6, 18, 26
Gd IV	10	Os VIII, IX	8	Cm II	18, 26
Tb I, II, III	5	Ir IX, X	8	Bk I, II	6, 18, 26
Tb IV	13	Pt X, XI	8	Cf I, II	6, 18, 26
Dy I	6, 29	Au III	11	Es I, II	17, 18, 26
Dy II	6	Au IV	5		
Dy III	8, 13	Au V	11		

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W. C. MARTIN

Chairman of the Committee

COMMITTEE 5: MOLECULAR SPECTRA

A. *Compendia, Bibliographies and Atlases*

The literature of molecular spectroscopy has proliferated very rapidly during the reporting period. The impact of molecular lasers on the general field of chemical physics, together with the powerful potential applications of molecular spectroscopy in atmospheric physics, astrophysics, and environmental problems have stimulated much of this growth. In this short report it is impossible to make a definitive literature review. Important trends are however indicated. Literature citations in the following sections have been principally compiled from reports from individual workers in centres of research in molecular spectroscopy. The bi-monthly *Berkeley*

Newsletter (1), compiled by Phillips and Davis from more than 30 journals, continues to be distributed to a mailing list of more than 500 workers. It is the most valuable source of rapid access to the literature of the spectra of small molecules. More than 100 *Newsletters* have been published, recent copies are about 20 pages in length and reference between 200 and 300 papers, books, etc. Suarez (2) announces a computer-consolidated bibliography on the spectra of diatomic molecules covering 1960 to 1970 based on the Berkeley Newsletter.

The very rapid recent proliferation of spectroscopic data has caused a great need for critical assessment of the published data in the literature and for the production of definitive compilations of reliable molecular data. Principal among these compilations is the work edited by Rosen (3) *Spectroscopic Data Relative to Diatomic Molecules* to which reference was made in the last report. This work has now been supplemented by a continuing series *Diatomic Molecules, A Critical Bibliography of Spectroscopic Data* edited by R. F. Barrow (4). Volume 1 was published in 1973. Barrow reports that Volume 2 is planned for 1975. A deliberate attempt has been made in Volume 2 to include data of astrophysical importance. Huber and Herzberg report that their extensive revision of the molecular data tables in Herzberg's text on the spectra of diatomic molecules is nearly complete and will be published shortly as a separate volume. Gaydon reports that work continues on the 4th edition of *The Identification of Molecular Spectra* by Pearse and Gaydon which will be ready shortly. Reference should be made to *Table of Band Features and Diatomic Molecules in Wavelength Order* by Jansson *et al.* (5), and to *Spectroscopic Data of Heteronuclear Molecules Parts A and B* edited by S. N. Suchard (6). Recent definitive reviews of molecular spectroscopic data cover the electronic spectra of CO (7) and O₂ (8) and the microwave spectra of formaldehyde, formamide and thioformaldehyde (9), methylenimine (10), methanol (11), hydrogen sulphide (12), water (13), OCS and HCN (14), CO, CS, and SiO (15) and SO (16). An extensive tabulation of microwave spectral data for 83 diatomic molecules has been published (17). The annual reports from Lagerquist's laboratory at Stockholm are very useful for assessment of ongoing research on many diatomic molecules. Nicholls and his collaborators at CRESS York University continue to produce Identification Atlases of Molecular Spectra and Spectroscopic Reports on Franck-Condon factors and Atmospheric Transmissions. Useful books which have appeared are (18–24). Gaydon (22) discusses numerous astrophysical spectra, and Thorne (23) has a good discussion on methods of spectroscopic intensity and *f*-value measurement. The Specialist Reports on Molecular Spectra of the Chemical Society of London contain authoritative review articles.

B. Molecular Data

The need for high quality molecular data for very high resolution laser applications, and frequent computer simulation of molecular spectra, together with the increasing use of measured spectral lines to provide input for numerical determination and molecular potentials and other molecular properties has revealed severe inadequacies in many existing molecular data and the methods by which they are obtained through analysis of molecular bands. The traditional methods of band analysis to determine molecular structure constants through the use of graphical and other techniques based on combination differences have been critically examined in an important set of papers by Albritton, Zare, and colleagues (25–29). These papers lay the quantal and statistical bases of suggested new methods of band analysis and study rotational analyses of band systems in O₂. One of the principal recommendations of this work is to use soundly based statistical and numerical analytical methods in the interpretation of molecular wavenumbers that give appropriate weighting to the data involved. The computer programmes developed in these very important studies are being increasingly used in a number of laboratories. Recent computer based Loomis-Wood branch analysis of many bands of the O₂ Schumann-Runge system of O₂ of Creek and Nicholls (30) is an example of similar work in which constants which describe the whole spectrum have been produced. Many spectroscopic data in the literature have been derived from the analysis of relatively few bands of each band system and are not always representative of a complete spectrum. Synthetic computer-generated molecular spectra have been increasingly used to simulate for example stellar spectra, auroral spectra, atmospheric transmission spectra and laboratory spectra. Such spectra take full account

of the location of all band-lines, their relative intensities and shapes. To do so very reliable molecular wavelength and intensity constants (Hönl-London and Franck-Condon factors) are needed. A continuing study has been made of them in a number of laboratories. One very encouraging trend in theoretical work of the reporting period is the very great improvement of *ab-initio* quantal calculations of the properties of many diatomic molecules. During the past year there have been significant increases in the capability of such work to predict molecular potentials, molecular dissociation energies and many other molecular constants almost to the precision of measurement. Important developments have been made at the NASA Ames Research Center, at the Argonne National Laboratory and at the IBM Research Center, San Jose. The work reviewed below is principally that reported by individual authors.

I. *Electronic Band Analyses and Constants for Diatomic Molecules*

Tatum (Victoria) reports on a new ($^1\Pi$) state of ZrO and rotational analyses of the (0, 0) band of $^1\Pi - X^1\Sigma^+$ system and of the $\Delta v = 0$ sequences of the ($A^3\Phi - X^3\Delta$) system. Bands of both of these have been found in S stars (31). He also reports studies on the CN violet system in Comet Bennett (32) and is currently working on TcO. Barrow (Oxford) reports that emission bands tentatively attributed to a new $^1\Sigma^- - ^1\Sigma^-$ transitions of SiO have been shown to arise from $E^1\Sigma^+ - X^1\Sigma^+$ of SiO (33). Loftus (Oslo) reports on work on corrections to spin-orbit coupling constants (34) and on centrifugal parameters of the electronic and microwave spectra O₂ and SO (35, 36). He and his colleagues are actively engaged in research on the calculation of model-independent term values from observed spectral lines using a statistical approach on bands of CH and CH⁺ (37) and on C₂ (38). Creek and Nicholls (Toronto) (30) have made definitive re-analyses of the constants of the O₂ Schumann-Runge system. Danylewych and Nicholls report extensive excitation of many ClO A-X bands on which vibrational and rotational analyses are in progress. Albritton (Boulder) reports, in addition to the development of a statistical method of band analysis (27) that he is collaborating with the Crosswhites (Argonne) on the analysis of the A-X system of the OT molecule. Crosswhite is making similar studies on OH. Leach and Rostas (Paris) report rotational analyses on the A-X spectra of OH⁺ and OD⁺ (39). Analyses are also in progress on the similar band systems of SH⁺, SD⁺, CS⁺ and CS. Ramsay (Ottawa) reports studies with McKellar on the infrared absorption bands of HD and on an extensive revision of his earlier analyses of the ClO spectrum. Weniger (Meudon) reports on studies on the rotational vibration analyses of the first negative bands of the isotopic CO⁺ ($^{13}\text{C}^{18}\text{O}^+$, $^{12}\text{C}^{18}\text{O}^+$, $^{12}\text{C}^{16}\text{O}^+$) (40). Lindgren and Lagerquist (Stockholm) report a continuing extensive research programme on the spectra of many diatomic species, many of which are astrophysically important. Work is in progress on N₂ and N₂⁺ (41–43), SiO (44–47), CH and CH⁺ (48, 49), ZrO (50), FeH (51), CuO (52, 53), CaH (54–57). Miescher (Basel) reports analyses of high resolution absorption spectra of $^{14}\text{N}^{16}\text{O}$, $^{15}\text{N}^{16}\text{O}$ in the 1250–1400 Å range, and of an emission spectrum (3dδ–3pΠ) of NO in the visible and near infrared under lasing conditions (58–62). Gaydon (London) reports analysis of a band of TiH (63). Weissler (Los Angeles) reports a continuing programme of research on the vacuum ultraviolet spectra of molecules in collaboration with the late Prof. M. Ogawa and other colleagues. He reports analyses of spectra of CO, O₂ and O₂⁺ (64–70). Callomon (London) reports work on AsO and ClO. Linton (Fredricton, New Brunswick) reports rotational analyses of TiO spectra (71).

II. *Transition Probabilities, Lifetimes, Intensities*

Among the major theoretical developments have been improvement of *ab initio* calculations to the level where agreement between experimental observations and theoretical predictions are becoming sufficiently good as to encourage belief in theoretical predictions in the absence of experimental data. There have also been a number of important calculations on line strengths (Hönl-London factors) and Franck-Condon factors (including the effect of molecular rotation) and *r*-centroids. Many emission and absorption intensity measurements have been interpreted in terms of band strengths, band oscillator strengths and similar quantities. This work has been aided by the use of synthetic spectral interpretation. Important observations have also been

made on molecular lifetimes and on the dispersive properties of molecular gases (refractive indices) in the vacuum UV. Weissler (Los Angeles) reports on measurements by his colleagues Ogawa, Lee, Judge and Carlson on absorption cross-sections and electronic transition moments of band systems of N_2 , O_2 , CO , CO^+ , N_2^+ (72–77). Smith (Princeton) and colleagues have measured oscillator strengths, lifetimes and electronic transition moments for SiO , SiO^+ , CH , CH^+ , SiH^+ , H_2 , D_2 , OH and OD (78–85). Parkinson and Smith (Harvard) report on refractive index measurements on H_2 , CO , O_2 and air between 1680 and 2880 Å. Penner (La Jolla) reports a continuing shock tube spectroscopy programme on the measurement of oscillator strengths of metal oxide spectra (86). McGregor (New Brunswick) reports new shock tube measurements on the oscillator strength of the $MgH A^2\Pi-X^2\Sigma^+$ system (87). Lindgren (Stockholm) reports lifetime measurements on SiO (85), NO (88) and OH^+ , SH^+ and NH^+ (89). Marr (Reading) reports on photoelectron spectroscopy on N_2 and CO using the Daresbury synchrotron as a vacuum UV light source (90, 91). Thorne (London) reports a continuing programme on 'hook-method' oscillator strength measurements on MgH and CaH bands. Hefferlin (Tennessee) continues his programme of critical assessment literature reports on molecular oscillator strengths, lifetimes and transition moments. Klemsdal (Tromsø) published a valuable compilation and critique of molecular transition moment data (92). Schadee (Utrecht) reports theoretical studies on energy level location ($J < \Lambda + S$) and Hönl-London factors for $^3\Pi-^3\Sigma$ transitions for arbitrary coupling cases have been calculated (93). He also has work in progress on the Zeeman effect on diatomic lines. Docken and Guberman (Harvard) report theoretical studies on photoionization cross sections for astrophysically important molecules and on absorption of radiation by O_2 and autoionizing states of H_2 (94, 95). Broida (Santa Barbara) reports intensity measurements on spectra of FeO (96), chemiluminescence of AlO and laser luminescence of TiO .

III. Polyatomic Molecules

Callomon (London) reports continued work on N_2O^+ and CO_2^+ . King (Hamilton, Ontario) reports recent analyses of the electronic absorption spectrum of thioformaldehyde (97), carbonyl selenide (98) and selenium dioxide (99). Weissler (Los Angeles) reports work on photoionization cross sections for CO_2^+ (100, 101). Leach and Rostas (Paris) report a rotational analysis of CO_2^+ bands (102). McBride and Nicholls (Toronto) report vibrational and rotational analyses for the principal vibration bands of ammonia (103, 104). Ramsay reports extension of his earlier analysis (with Dressler) of NH_2 bands.

RESEARCH IN PROGRESS

A. From the National Research Council of Canada

(reported by G. Herzberg and A. E. Douglas)

Spectroscopic work at Ottawa is going on in the optical infrared and microwave regions, and theoretical studies on topics in molecular spectroscopy are being carried out. The ultraviolet spectrum of D_2 and HD has been studied in considerable detail (105–107). The rotational and vibrational levels of the ground state derived from these studies agree in a remarkable way with the results of *ab-initio* calculations. The intensities of the infrared bands of HD have been studied (108, 109) and the spectrum has been extended to the sixth overtone, that is, the 7–0 band (110). The significance of pressure shifts for the interpretation of the H_2 quadrupole lines in planetary spectra has been considered (111). Absorption and emission spectra of HF and F_2 have been investigated in the ultraviolet and precise values for the rotational and vibrational intervals in the ground state nearly up to the dissociation limits have been obtained (112, 113). A new absorption band of OH in the 1200 Å region has been described (114). Other diatomic molecules studied are CaH (115), SiI (116), $BeCl$ (117) and N_2 (118). The spectra of molecular ions continue to be studied in this laboratory. The work on C_2^+ (119) and NO^+ (120) has been

published and the work on H_2O^+ is nearing completion (121). The H_2O^+ ion has been observed to be a prominent feature in the spectrum of Comet Kohoutek, as predicted in the 1973 report (122). More recently, a new spectrum connected with NH_3 has been observed which is likely to be due to the NH_2^+ ion (123).

Studies of neutral polyatomic molecules in the microwave region have continued. Of astro-physical interest are the studies of NH_3 (124–126), HCN (127), CH_4 (128–130), H_2CS (131) and H_2CO (132). For some of these the effects of individual collisions have been studied by double resonance methods, and in others, like CH_4 , forbidden transitions have been observed by radiofrequency-infrared double resonance. A review on collision-induced transitions between rotational levels has been published (133). Infrared spectra of methane have been studied with very long absorbing paths and the Kuiper bands of Uranus have been thus identified (134). Other infrared spectra of possible astronomical interest which have been studied are those of formaldehyde (H_2CO) (135), diimide (N_2H_2) (136) and ketene (CH_2CO) (137). In the visible, ultraviolet and vacuum ultraviolet, discrete absorption and emission spectra of H_2CO (138), SO_2 (139), NO_2 (140–142), HNO (143) and N_2H_2 (144) have been studied, leading to detailed information about some of the excited states of these molecules. The observed predissociation in the spectrum of H_2O in the vacuum ultraviolet may be responsible for the inversion in the ground state that leads to the H_2O laser emission in interstellar clouds (145). Other polyatomic molecules studied in the ultraviolet are HSiI (146), PH_2 (147), C_2HCHO (148–150) and CO_2 (151). Reviews on microwave spectra (152) and vacuum ultraviolet spectra (153) have been published.

B. *From the Planetary Sciences Section, Herzberg Institute of Astrophysics*
(reported by A. Vallance Jones)

Our work is primarily in the field of the observation and interpretation of auroral and airglow spectra. Considerable progress has been made in the quantitative measurement of the auroral spectrum from 3150 Å to 11 500 Å using a digital scanning spectrometer and appropriate photomultipliers (154–156). The problem of the excitation of $\text{O}_2(^1\Delta)$ has been demystified by ground observation of the growth and decay of the emission relative to the excitation intensity in several auroral substorms (157). On the other hand, the detection of O_2 atmospheric bands with $3 \leq v' \leq 5$ suggests that $\text{O}_2(b^1\Sigma)$ may be excited by some mechanisms other than $\text{O}(^1\text{D})-\text{O}_2$ energy transfer (158). In the field of pure molecular spectroscopy our most interesting achievement has been the almost complete synthesis of the auroral spectrum as described in (154–156). In order to match the O_2^+ 1st negative bands to the observations an empirical determination of the parameters of the intermediate coupling case between case (a) and case (b) was initially employed; theoretical line strength factors provided by R. N. Zare were later incorporated. This has recently been shown to be in good agreement with laboratory spectra.

C. *From the National Bureau of Standards*
(Reported by Donald R. Johnson)

Laboratory work on the microwave spectra of a variety of new molecules with potential for interstellar investigations is continuing in the NBS laboratories. Lovas *et al.* have detected and analyzed the microwave spectrum of S_2O_2 , a strongly polar dimer of the SO radical (159). Vinylamine, CH_2CHNH_2 , has been isolated and analyzed by Lovas *et al.* (160). Both the *cis* and *trans* forms of methylideneimine, CH_3CHNH , have been identified and analyzed in detail by Lovas, Clark, and Johnson. Maki and Johnson have completed a detailed study of the microwave spectrum of vibrationally excited carbonyl sulfide (OCS) (161). Laboratory measurements of the frequencies of the C-13 isotopic species of methanol (CH_3OH) have been made by Haque and Lees (Univ. of New Brunswick), and Saint Clair and Beers (NBS Boulder) and Johnson (162).

A series of critical reviews of laboratory microwave spectra of interstellar molecules has been

initiated at NBS in collaboration with individuals from a variety of other institutions. The reviews (9–16) mentioned above have been published. A review of the laboratory spectrum of acetaldehyde (CH_3CHO) which includes extensive new measurements and a complete reanalysis has just been completed by A. Bauder (Swiss Federal Institute), Lovas and Johnson (163). Similar reviews of dimethyl ether (CH_3OCH_3) by H. Dreizler (University of Kiel), Lovas and Johnson, isocyanic acid (HNCO) by M. Gerry (University of British Columbia), W. Hocking and G. Winnewisser (Max Planck Institute, Bonn), the hydroxyl radical (OH) by R. Beaudet (University of Southern California), and silicon monosulfide (SiS) by E. Tiemann (Free University of Berlin) are nearing completion. Lovas is preparing a tabulation of microwave data on triatomic molecules similar to that (17) for diatomic molecules. It is about 80% complete and will include a complete predicted spectrum of SO_2 for astrophysical and calibration purposes.

A laser magnetic resonance study of the HO_2 molecules has yielded molecular constants for the ground electronic and vibrational state which include three rotational constants, three centrifugal distortion constants, and three spin-rotation splitting constants (164). The vacuum ultraviolet emission spectrum of CO in the 950–2100 Å region has been re-examined. Several bands previously assigned to CO are shown to originate from molecular nitrogen (165). High resolution spectra of the $\nu_1 + \nu_3$ band of ozone (O_3) have been obtained and assigned by Maki (166). Krell and Sams have made an exhaustive study of the rotation-vibration bands of N_2O which fall in the 4.1 μm region (167). A number of NO_2 bands has been studied by R. L. Sams, W. J. Lafferty, and collaborators. These include the fundamentals ν_3 (168, 169) and ν_2 (170) as well as the overtone or combination bands $2\nu_3$ (171), $2\nu_1$ (172) and $\nu_2 + \nu_3$ (172). Work is in progress on the $\nu_1 + \nu_2$ and $2\nu_2 + \nu_3$ NO_2 bands. Several Q-branch lines have been assigned in the spectrum of the ν_3 band of $^{15}\text{N}^{16}\text{O}_2$ by Freund *et al.* using laser magnetic resonance techniques (173). Values for the band center and the vibrational change in the A rotational constant have been derived. Maki (174) has recorded and analyzed the spectrum of HCN in the 3 μm region at elevated temperatures (up to 1000 °C).

D. *From the University of California, Berkeley*

(Reported by J. G. Phillips and S. P. Davis)

I. *Rotational Analyses*

ZrO. Current research concentrates on detailed analysis of bands in spectra of ZrO in the spectral range from 3600 Å to 9600 Å. Fourier transform spectral studies in the infrared are planned. Spectra are taken of the three isotopes Zr^{90}O , Zr^{94}O and Zr^{96}O . Dispersions range typically from 0.34–0.8 \AA mm^{-1} . The current arc source will eventually be supplemented by a lower temperature electric furnace source. Analyses are in various stages of completeness on 22 bands in the three known triplet systems, and the search for further bands in these systems is continuing. The 5860 Å band of ZrO is found to be the O–O band of a new $^1\Sigma^+ - X^1\Sigma^+$ transition. Additional bands of the system have R heads at 5893 Å, 5926 Å and 5961 Å. A weak rotational perturbation in the 5860 Å band has been shown to be produced by coincidences with rotational states of the $v = 2$ vibrational level of the $^1\Pi$ electronic state. A new $^3\Pi - X^3\Delta$ system has been partially analyzed at 9299 Å. It appears strongly in the spectrum of S-type stars. The great complexity of the ZrO spectrum in this region probably means that two or more systems are superimposed, but we have succeeded in finding two sets of R and Q branches that lead to combination differences agreeing with those for $v = 0$ of the $X^3\Delta$ state. This confirms the theoretically predicted existence of a previously unobserved $^3\Pi$ state in the energy-level diagram of ZrO. A great amount of time has been devoted to an attempt to identify the transition responsible for the 8192 Å band that is quite prominent in the ZrO spectrum. Tentative analysis and isotope shifts show that it is a O–O band of a ZrO transition, probably between singlet states, although we cannot rule out the possibility that it might be due to a singlet-triplet intercombination. However, rotational constants derived from any reasonable

branch assignment are much smaller than expected for ZrO, and combination differences do not fit with those of any known ZrO system. At present this band is a mystery.

CN, C₃. The Fabry-Pérot scanner has been used to detect the fundamental vibration-rotation band of CN produced by a King furnace, and its oscillator strength has been estimated. In addition, a strong feature at 5 μm is seen in the spectrum of the hot carbon furnace, which has been tentatively attributed to a fundamental band of C₃.

II. Transition Probabilities

A tunable dye laser is being applied to the measurement of the lifetimes of excited states of TiO. Fluorescence is being observed in the rotational structure in the 0-0 band of the β-system produced in the electric furnace. The rotational and vibrational constants derived from our ZrO analysis are being applied to the construction of synthetic band profiles for comparison with photoelectric scans of furnace spectra for the calculation of relative transition probabilities.

E. From the Physics Dept., University College Dublin

(reported by P. K. Carroll)

Work is continuing on the spectra of transition metal hydrides. New wavelength tables of the FeH spectrum, reported earlier (175), have been made and the evidence for its presence in the solar spectrum, both disc and spot, has been strengthened. A new band at 8 689.8 Å degraded to longer wavelengths has also been measured. In MnH another transition at 10 600 Å has been found. The analysis of the far UV absorption spectrum of N₂ under high resolution has been continued (176-178) with particular reference to Rydberg states. Emission studies in the near UV involving Rydberg states (179) have also been carried out and a new state, $k^1\Pi_g$, has been found (in press). The absorption spectrum of P₂ has been studied in the vacuum region between 1370 and 600 Å (180). Many Rydberg states have been observed, the ionization potential of the molecule has been accurately determined and the relative energies of the known states of P₂⁺ have been established. New studies on the atomic spectra P I and P II have been made in the vacuum ultraviolet and the autoionizing 3s3p³np ⁴P levels of P I have been observed. The spectra of some lighter elements excited in laser induced plasmas have been studied at various wavelengths. In the grazing incidence region the resonance series of B IV and B V together with their associated ionization continua have been recorded.

F. From the Centre for Research in Experimental Space Science, York University, Toronto

(reported by R. W. Nicholls)

The experimental and theoretical research programme for the provision of transition probability and structure data for molecular spectra of astrophysical interest continues. Critical assessments have been made of molecular structure constants of NH₃ (103, 104), O₂ Schumann-Runge (30) and C₂O (181). New analyses have been made for NH₃ and O₂, and are in progress for C₂O. Absolute band strength measurements have been made in absorption, using the hook method, on NO band systems (182-185). Shock tube spectral radiometric methods, which incorporate the use of synthetic spectral techniques, have been used in emission to determine the electronic transition moment of the CN Red system (186) and of the CN Violet system (187) during which the dissociation energy of the X²Σ state of CN was also determined. Similar shock tube radiometry has been used to determine the electronic transition moments (188) and band strengths (189) of the C₂ Swan, Deslandres-d'Azambuja, Mulliken, Freymark, Ballik-Ramsay, Phillips and Fox-Herzberg systems. An extensive set of intensity measurements in emission of the C₂ Swan system has been analyzed by synthetic spectral methods to determine the variation of the electronic transition moment with internuclear

separation and to provide a complete table of band strengths for the C₂ Swan system (190, 191). Identification atlases for NO₂ and SO₂ are in preparation. The synthetic spectral programme SPECT3 has been developed and refined for the interpretation and prediction of laboratory and atmospheric spectra (192, 193). Definitive studies have been made of the theory of rotational line strengths (Hönl-London factors) (194). A comprehensive computer programme has been developed for the evaluation of the line strengths and to correct previous tabulations of them (195). Extensive tables of Franck-Condon factors, *r*-centroids and figure of merit factors appropriate to realistic numerical molecular potentials have been computed for more than 200 band systems and 10⁵ bands. Some of these data have been issued during the report period (196). Study of determination of Franck-Condon factors by interpolation methods has continued (197). Studies of the mathematical bases of the *r*-centroid approximation continue (198–201).

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