

14. COMMISSION DES DONNEES SPECTROSCOPIQUES FONDAMENTALES

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3. Committee on Molecular Spectra.

Chairman: J. G. Phillips.

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GENERAL COMMENTS

The responsibility of Commission 14 is increasing so rapidly that an appraisal of the present activity and future trends may be in order. The Commission is unique in its basic purpose, namely, to provide a strong liaison between astronomers and laboratory spectroscopists. In the United States, at least four data centers exist primarily to provide critical data of astrophysical interest: (1) Atomic Energy Levels and (2) Transition Probabilities (both at the National Bureau of Standards, Washington, D.C.), (3) Cross Sections (Joint Institute for Laboratory Astrophysics, Boulder, Colorado); (4) Diatomic Molecules (University of California, Berkeley, California).

Other problems are coming into the foreground, such as the use of lasers in precision spectroscopy—a topic suggested by a number of our members. The coupling of astrophysical needs with laboratory programs is one of our prime obligations.

ACTIVITIES OF THE COMMISSION

Since the 1964 General Assembly the Commission has acted as sponsor for three symposia:

1. In Trieste, 13–15 June, 1966, the IAU was represented by President Swings, and the Commission by Mrs Moore-Sitterly as co-sponsor of a colloquium on Late-Type Stars. This was organized by Mrs Hack, Director of the Trieste Observatory.
2. In Boulder, Colorado, 11–15 July, 1966, the Commission sponsored a Colloquium on Atomic Collision Processes, which was well represented by a number of our members under the leadership of Seaton (see below).
3. In Bombay, India, 9–18 January, 1967, an International Conference on Spectroscopy was organized by Asundi and attended by Herzberg and Mrs Moore-Sitterly as representatives of Commission 14.

Two International Commissions require representation from Commission 14.

1. The Triple Commission for Spectroscopy has served to coordinate the needs and efforts of the three International Unions, Physics, Chemistry, and Astronomy, in the field of spectroscopy. In 1964, this Commission convened in Hamburg immediately after the Twelfth General Assembly of the IAU. At this meeting progress reports on atomic and molecular spectra were presented with detailed bibliographies (388)*.

At the next meeting, held in Copenhagen, 19 August, 1965, it was decided to reorganize the TCS. Since two of the three International Unions concerned have Spectroscopy Commissions (IUPAC and IAU) it was recommended that IUPAP should, similarly, form its own Spectroscopic Commission in order to have three 'parallel' Commissions, one for each Union. It was proposed that each Union name four members to serve on the TCS. For the IAU the representatives will be: Edlén, Mrs Moore-Sitterly, Phillips, and Seaton. The normal term of service will be six years. In order to preserve continuity it was suggested that each group of four select two to serve only three years.

The function of the TCS as reconstituted will be to decide on matters of concern to the three International Unions and to coordinate the work of the three separate Commissions.

2. At Unesco House in Paris, 16–17 June, 1966, an ICSU Committee on Data for Science and Technology was established, with Harrison Brown as Chairman *pro tem*. This committee is made up of both National and Union Representatives. The President of IAU Commission 14 is the IAU Representative. Rossini was chosen as President, Klemm and Vodar as Vice-Presidents, and Sutherland, Secretary-Treasurer. Further information can be obtained from the office of the Executive Director, Guy Waddington, 2101 Constitution Ave., N.W., Washington, D.C., 20418, (U.S.A.). The Reports of Commission 14 furnish much useful data and reference material for this ICSU Committee.

STANDARDS OF WAVELENGTH

(Committee 1)

B. Edlén

The metrological properties of the He-Ne laser radiation, with the approximate vacuum wavelength 6329.914Å , are being investigated at NBS (315a), NRC, NPL (404a) and PTB (135a). The results indicate that this radiation is likely to become an exceedingly useful secondary standard for length measurements.

*Reference numbers in parentheses refer to the general bibliography which follows the report of the Commission.

Work on the determination of line profiles of selected Hg 198 and Kr 86 lines, advocated at the 1964 meeting of this Committee, is reported by Terrien (BIPM) and Rowley (NPL). The results from BIPM and NPL agree on the existence of a small but detectable asymmetry in all the investigated Kr 86 lines, similar to the one previously found in the Kr 86 primary standard line. Terrien found (452a) that the asymmetry was independent of all changes made in the experimental arrangements, and that it could be described in terms of a faint satellite about 0.007 cm^{-1} to the longwave side of the main line. No explanation for the asymmetry has been offered. We wish to point out, however, that approximately this kind of asymmetry would be expected from a small admixture of Kr 84.

Engelhard further reports that, after having studied the original laboratory records of Kösters and Lampe, he has revised their formula for the refractive index of air, whereby the difference with the formula of Barrell and Sears is reduced from 9 to 6 units in $(n - 1) 10^8$. A comprehensive review of our present knowledge of the refractive index of air, published by Edlén (134), includes an improved dispersion formula for standard air, as well as formulas for the dependence of refractivity on temperature and pressure and on relative contents of CO_2 and H_2O . Since the differences between the new dispersion formula and that of 1953 are very small, it was suggested that a replacement of the 1953 formula as standard in spectroscopic work would not be necessary for the time being. Regarding the absolute values of the refractive index it was concluded that there are as yet no definite indications that the values adopted in 1953 should be changed, but new experiments aiming at reducing the present uncertainty of $\pm 5 \times 10^{-8}$ would be desirable.

Rare Gas Standards

The results of measurements on 37 Kr 86 lines from 6458 to 4264 Å, made at the NPL and previously reported to this Commission, have been recalculated by Cook (96) to give wavelengths as observed through the anode end of an Engelhard lamp. These values are compared with those previously obtained by Kaufman and by Phelps, and it is estimated that means of the three sets of data may be relied upon to 0.0001 Å.

Humphreys and Paul (225) have communicated for this Report the results of photographic interferometer measurements on selected lines, mainly in the infrared, in the spectra of Kr 86 and Xe 136 (Tables 1 and 3). Provisional values for the $1s$ and $2p$ terms which they have derived from these measurements are shown in Tables 2 and 4. Microwave-excited electrodeless tubes were used as light sources, and the Hg 198 lines at 4047.7147 and 4359.5625 Å, supplemented by some argon wavelengths, served as standards. When comparing the new Kr 86 wavelengths with those reported in 1964 to this Commission by Littlefield and Sharp one finds a systematic difference, the new values being about 0.003 Å lower.

Interferometric measurements on 84 lines of Ar I and 69 lines of Ar II, in the region 5000–7000 Å, have been completed by Norlén (343a) at Lund. The light source was a water-cooled hollow cathode, the Fabry-Pérot etalons ranged up to 49 mm, and as reference line served the Kr 86 line at 6057 Å, produced by a microwave-excited electrodeless lamp obtained from the PTB. The error limits are estimated to ± 0.0004 Å. When comparing the results with the two previous sets of interferometric measurements on Ar I lines in this region (both from 1953) one finds no significant systematic difference with Littlefield and Turnbull, while the values of Burns and Adams are on the average 0.002 Å larger.

Table 1. ^{86}Kr I vacuum wavelengths

(1966 interferometric measurements by Humphreys and Paul)

4275.1716	7696.6568	8115.1306	8300.3880
7589.5005	7856.9828	8192.3055	8511.2072
7603.6375	8061.7200	8265.5111	8779.1576
7687.3590	8106.5929	8283.3254	8931.1424

†

Table 2. Energy levels of $^{86}\text{Kr I}$
(Humphreys and Paul, 1966)

$1s_5$	0.0000	$2p_{10}$	11 196.7759*	$2p_4$	17 624.1762
$1s_4$	945.0243	$2p_9$	12 322.6605*	$2p_3$	17 947.4074
$1s_3$	5219.8755	$2p_8$	12 335.6386	$2p_2$	17 973.4277
$1s_2$	5874.9615	$2p_7$	12 992.6540	$2p_1$	18 883.3301*
		$2p_6$	13 151.6002		
		$2p_5$	14 121.1219*		

*Only one interferometrically observed combination available for evaluation.

Table 3. $^{136}\text{Xe I}$ vacuum wavelengths
(1966 interferometric measurements by Humphreys and Paul)

4502.2424	4735.4775	7969.5326	8282.3956	8821.8359
4525.9510	4808.3635	8063.5534	8349.1198	8864.7497
4625.5719	4917.8799	8208.5947	8411.5043	8954.7131
4672.5344	7644.1300	8233.9003	8650.8817	9047.9337
4698.3365	7889.5649	8268.7944	8741.7743	9165.1711

Table 4. Energy levels of $^{136}\text{Xe I}$
(Humphreys and Paul, 1966)

$1s_6$	0.0000	$2p_9$	11 052.2472	$2p_4$	21 311.5744
$1s_4$	977.6092	$2p_8$	11 335.5089	$2p_3$	22 094.8038
$1s_3$	9129.2210	$2p_7$	11 888.4800	$2p_2$	22 211.1544
$1s_2$	10 117.4932	$2p_6$	12 144.9127	$2p_1$	22 792.4634
		$2p_5$	13 051.4106		

Thorium Standards

The measurements by Littlefield and Wood, previously reported to this Commission, have now been published (287a). Giacchetti, at the Argonne Laboratory, has furnished a typewritten compilation and comparison of all the five sets of precision measurements on thorium lines that have been published up to this date. This compilation, which contains four-decimal wavelengths of 701 lines from 2566 to 9050 Å, will make it possible to extract a list of wavelengths measured with consistent results by two or more observers and thus being acceptable as standards.

Vacuum-ultraviolet Standards

Substantial progress has recently been achieved regarding wavelength standards in the vacuum ultraviolet. This is largely due to the efficient use of the NBS 10.7 m vacuum spectrograph in the hands of Kaufman and Ward. In the case of Ni I, these authors (246) have derived calculated wavelengths, accurate to 0.001 Å or better, for 78 lines from 908 to 1745 Å, based on their measurements of the multiplets at 1492 and 1742 Å combined with Eriksson's (136b) measurements of the forbidden transition at 3466 Å. The same authors (245) have checked the suitability of calculated Cu II standards and have revised the value of the ground level a^1S_0 , which permits a considerable extension of available Cu II standards toward shorter wavelengths. In the same paper they report precision measurements of some key multiplets which lead to revised values of the calculated wavelengths for Si II (Table 5) and Ge II (Table 6) and confirm the C I wavelengths calculated by L. Johansson (231a).

A paper on Si I by Radziemski, Andrew, Kaufman and Litzén (391) gives the final values of low-pressure-source levels as well as recalculated wavelengths of 100 lines and measured wavelengths of 41 lines, thus covering the region from 1991 to 1560 Å with standards accurate to 0.0016 Å or better.

Wavelengths of the Lyman lines, $1s - np$, have been calculated for the spectra from H I to Si XIV by Edlén and Svensson (132) in connection with their redetermination of the X-unit. The values for Be IV through Si XIV were later revised (133) in view of the information given by Garcia and Mack in an exhaustive treatise on levels and wavelengths of the spectra from H I to Ca XX (168). This important work by Garcia and Mack represents an all out effort to push the accuracy of these data to the limit set by our present knowledge of the atomic constants and by the present state of the theory of one-electron spectra.

Table 5. Si II vacuum wavelengths (calculated)
(Kaufman and Ward)

820.9210	889.7228	1023.7002	1260.4212	1526.7073
822.8613	899.4063	1190.4157	1264.7374	1533.4319
843.7192	901.7359	1193.2894	1265.0010	1808.0125
848.0700	989.8730	1194.5001	1304.3716	1816.9283
850.1409	1020.6988	1197.3936	1309.2772	1817.4512

Table 6. Ge II vacuum wavelengths
(Kaufman and Ward)

Calculated	Calculated	Calculated	Calculated	Measured
843.7165	905.9771	1017.0600	1576.8547	1938.0077
856.4880	920.5537	1055.0261	1581.0698	1938.8906
862.2339	920.7195	1075.0720	1602.4863	1979.2736
872.3075	926.4736	1237.0589	1649.1942	2007.6883
875.4927	941.8962	1261.9053		
875.5766	999.1011	1264.7096		
885.9663	1016.6377	1538.0907		

TRANSITION PROBABILITIES

(Committee 2)

Work in this field is so active that no attempt will be made to cover it completely. The existing data centers maintain current reference files from which information can be obtained.

Atomic transition probabilities. Wiese and his staff have published a critical compilation of atomic transition probabilities for about 4000 spectral lines of the first ten elements, H thru Ne, based on all available literature sources (485). Glennon and Wiese issued a current bibliography on this subject (182) in April 1966, which supersedes their Monograph 50, 1962.

Two survey articles may be mentioned. Foster (159a) has given a comprehensive account of the experimental methods for the determination of oscillator strengths, and Garstang (172a) has surveyed the period 1960-64.

I. Experimental Determinations of Transition Probabilities

R. B. King reports a continuation of work on oscillator strengths derived from absorption spectra. Relative values for 300 lines of Fe I have been published (254). The work by Moise on Transition Rates of Atomic Transitions, reported in 1964, has since been published (319).

Similarly, the earlier report on the absolute oscillator strengths of lines in the spectra of ten elements is now in print (283). The results by Link on lifetimes of upper states obtained by using the 'level crossing' technique has stimulated the effort to improve the earlier determinations of absolute f -values. Ashenfelter is using the atomic beam apparatus for this purpose.

In collaboration with Whaling, who has constructed an ion source capable of producing a beam of metallic ions, an attempt is being made to observe the rate of decay of Fe ions emitted in the second and third stages of ionization, as observed with a Van de Graff accelerator and carbon foil target. This work is in its initial stage, according to King.

Kuhn reports studies at Oxford of self broadening and pressure shift of lines in the visible and near infrared spectra of He (464), Ne, Ar (434), and Kr, observed by means of direct recording interferometers. Measurements of resonance broadening constants can be used to obtain f -values of strong resonance lines.

Peach has determined relative f -values of certain pairs of Fe I lines, with accuracies estimated from 2 to 15%. All lines have low excitation potentials, below 3.5 eV (370).

Garstang has stressed the importance of recent work on lifetime determinations. The method of phase shift has been used in some of the more important investigations of the last few years. Intensity modulated light is used to excite an atomic state, and the delay in the phase of the emission fluorescence is related to the lifetime of the state. Link (287b) has determined the lifetimes of the upper states of the resonance lines of Na I, K I, Rb I and Cs I, with results in good agreement with earlier work. Lawrence and Savage (283a) have worked on B I, B II, C I, C II, N I and N II. Cunningham and Link (unpublished) have measured several states in Na I, Tl I, In I, Cu I, Ga I, Ag I, Pb I and Bi I, and Savage and Lawrence (unpublished) have studied Si I, Si II, P I, P II, S I, S II, O I, Ne II and Ar II. The method has been applied also to molecules. A delayed coincidence technique was used by Klose in work on Ne I and he has done further work on Ar I.

Prokofiev has reported as follows: The lifetime of an excited state of Cs $7^2P_{3/2}$ has been determined by the double-resonance method (9). Lifetimes of some states of Hg and Cd have been determined by the delayed-coincidence method (471). Oscillator strengths in the spectra of Fe I (476), Al I and Ga I (376) and Cu I and Ag I (425) have been determined by the anomalous-dispersion method. Relative values of oscillator strengths in the spectra of Fe II (326), Ti I, V I, Cr I, Fe I, Co I and Ni I (325) have been determined by the radiation method. The transition probability of the Ne I line designated $2s_2 - 2p_4$ (118), oscillator strengths of Cu I (364), and resonance peaks of Xe I (82) have been determined by the absorption method. Use of the combined measurement of full and linear absorption in a layer of vapours formed in the heated graphite tray has made it possible to determine the absolute values of oscillator strengths of a number of resonance peaks of Bi I, Sb I and Te I (288). Lifetimes of the states H I with $n = 3, 4$ and 5 (11) have been measured by the method of excitation of a beam of high-velocity hydrogen atoms in helium.

Corliss has prepared a Supplement to NBS Monograph 32 on Spectral Line Intensities, which contains a calibration of some 1400 lines short of 2450\AA (102). In Ni I he has reduced relative intensities and oscillator strengths of 888 lines between 2800 and 9900\AA to absolute values (100). He and Warner have carried out similar work on 2000 lines of Fe I between 2080 and 4150\AA (101).

II. Theoretical Investigations of Oscillator Strengths

Czyzak, Krueger and others (105, 106) have done extensive theoretical work on the calculation of atomic wave functions, transition probabilities (allowed and forbidden), and cross sections which are primarily of astrophysical interest. Most of the wave functions have been used for determining transition probabilities for lines in selected spectra of P, S, Cl,

Ar, K, Ca, Cr, Mn, Fe and Ni in various stages of ionization extending as high as Ar xv, K xiv, Ca xv, Mn xiii, Fe xiii, Ni xvii.

In collaboration with the above authors, Aller and his associates have calculated oscillator strengths for some 50 transitions of astrophysical interest in Na I, Mg II, Al III and Si IV, by using Hartree-Fock self-consistent field wave functions with exchange (81). A. B. Underhill has carried out similar calculations of gf -values for 25 selected lines of Fe II, Fe III and Ni II by using both the Hartree-Fock and Bates-Damgaard methods (459).*

Treffitz reports work on wave functions and oscillator strengths of Be-like ions, C III, N IV, O V (381) and similar work taking into account configuration mixing for some Fe- and Be-like ions (437).

Very extensive calculations of screened hydrogenic wave functions, based upon Layzer's theory, have been completed by Naqvi and co-workers (333, 334). The screening parameters were calculated for the ground state and a large number of excited states along isoelectronic sequences with 2 (He) through 55 (Cs) electrons. The calculations for each isoelectronic sequence were done for twenty members, starting at the negative ion, in some cases. The screening parameters for still higher members can be determined by interpolation. Thus, calculations have been completed for a large number of atoms and ions of the periodic table, including moderately and highly ionized atoms.

These hydrogenic wave functions are currently being used to calculate allowed and forbidden transition probabilities. The results for some allowed transitions of the lithium, beryllium, boron and carbon isoelectronic sequences have been published (335) and others are in preparation. The calculations are done in intermediate coupling wherever appropriate. Work is also in progress on calculations of transition probabilities by using Hartree-Fock wave functions including configuration interaction.

Forbidden transition probabilities for ions of the nitrogen isoelectronic sequence (N I to Fe xx) have been calculated by Naqvi (336) in intermediate coupling by using Hartree-Fock wave functions with configuration interaction and also screened hydrogenic wave functions. There is good agreement between these two sets of calculations for multiply charged ions and this agreement improves as the ionic charge increases. The approximate screened hydrogenic wave functions are quite good for calculations of forbidden transition probabilities for ions with an ionic charge of four or more.

Prokofiev has also reported progress on theoretical work. A criterion of quantum defect, is suggested as useful for the application of a Coulombian approximation in calculating transition probabilities (197, 344): it has been used for calculating the oscillator strengths in the sharp and diffuse series of Al I, Ga I, In I and Tl I, as well as for resonance peaks in the isoelectronic series from He I to Ar I (343).

Transition probabilities have been calculated for the magnetic-dipole and other forbidden transitions in isoelectronic series, particularly in B I and Al I (343).

Garstang has discussed forbidden transitions in excitation by electron impact (170), with special emphasis on interesting transitions in He. Because of the astrophysical importance of Ba II, he and Hill have published all gf values for a number of Ba II lines (171). He has also calculated energy levels, oscillator strengths and transition probabilities for selected configurations and lines in the Fe xvii spectrum. This contribution is particularly useful to those who are interpreting the far ultraviolet solar spectrum (172).

Levinson and Nikitin (287) have published a convenient *Handbook for Theoretical Computation of Line Intensities in Atomic Spectra*.

For molecular spectra, a review of work on intensities and transition probabilities is given by Phillips (see §II p. 250).

*See Addendum on page 266.

SPECTRAL LINE BROADENING

(Committee 2a)

W. R. Hindmarsh

Of the causes of the broadening of spectral lines only Doppler broadening and the various types of 'pressure' broadening are important in astrophysical conditions. Doppler broadening is readily calculable if the velocity distribution of the emitting atoms is known; this report is concerned only with pressure broadening.

Considerable progress has been made in recent years in understanding the mechanism of broadening of spectral lines by collision between the radiating (or absorbing) atom and its neighbours. Weisskopf, as long ago as 1933, clearly appreciated the nature of the impact approximation, in which it is assumed that only the integrated effect over a collision on the phase and amplitude of the radiation matters; and of the quasistatic approximation, in which the perturbation of the frequency of the radiating atom by the fields due to neighbouring atoms is treated as though it were changing very slowly. The regions of validity of these approximations were early discussed by a number of authors, including Unsöld. The adiabatic theory of Lindholm and Foley was for some time the only available description which allowed numerical calculations in the impact approximation. Since then, the quantum mechanical formalism has been developed, especially by Baranger and Kolb and Griem; almost all numerical calculations have been based on the classical path approximation.

There are two distinct aspects of this problem—broadening due to interaction with charged particles (electrons and ions) on the one hand, and broadening due to interaction with neutral particles (atoms) on the other hand.

The theory of broadening due to charged particles has been greatly developed in recent years, especially by Griem and his collaborators, who were the first to include correctly the effect of collision-induced transitions. Earlier review articles by Böhm, Traving, Margenau and Lewis, Mazing, and Baranger, and more recent ones by Breene (50), van Regemorter (399), Wiese (484) and Griem (195) treat the subject in some detail. The last four discuss the influence of non-adiabatic collisions, and the last article includes extensive tables for calculation of the profiles (so far as they are determined by collisions with charged particles) of a large number of hydrogenic and non-hydrogenic ('isolated') lines of astrophysical importance. Comparisons between theory and experiment for broadening by charged particles have been reviewed by Baranger, Griem (195), Mazing and Wiese (484).

For hydrogenic lines a quasi-static theory, corrected for shielding effects (Ecker, Baranger and Mozer) is used for the broadening by ions. The quantum-mechanical non-adiabatic impact theory, including a correction due to Lewis, is used for the broadening by electrons. Approximate analytical expressions for the profiles of hydrogen lines have been given by Griem, although doubts have been expressed as to their validity for the electron densities and temperatures encountered in stellar atmospheres (Pfennig *et al.* (383)). The same difficulty seems also to be present in the work of Nguyen *et al.* (338). Griem's most recent wing formula (196a) is claimed to be free of these defects. For the lines $L\alpha$, $L\beta$, $H\alpha$, $H\beta$, and $H\gamma$, experiments carried out at rather high electron densities ($\geq 10^{16} \text{ cm}^{-3}$) and temperatures ($\geq 10^4 \text{ }^\circ\text{K}$) give satisfactory agreement with theory (195, 484), although Boldt and Cooper (44) did not find agreement with Griem's wing formula for $L\alpha$. Careful comparisons of theoretical and experimental profiles for high Balmer and Paschen lines have been made by Ferguson and Schlüter (152) and by Vidal (472) at electron densities of particular astrophysical interest (about 10^{13} cm^{-3}), and an electron temperature of about 2000°K . More recent work by Vidal (473), Pfennig *et al.* (383), Pfennig and Treffitz (382), Schülter *et al.* (414), Schlüter and Avila (415) and Edmonds *et al.* (135) reaffirms that the use of a quasi-static theory for electrons as well as ions gives good results whenever it is expected to be applicable as estimated by Unsöld.

These studies also include investigations deep in the impact regime for electron broadening (414), where the electron contribution is observed to be weaker than the quasi-static one. The most recent impact calculations by Griem show the same tendency, although the electron impact contribution observed at low electron densities seems to be definitely smaller than calculated (196a).

For non-hydrogenic lines the most important contribution is due to impact broadening by electrons; inelastic collisions are taken into account (Vainshtein and Sobel'man), (Griem, Kolb, Baranger and Oertel), (Bréchet and van Regemorter (49)). Experimental work has indicated that measured widths do not agree well with the earlier theories for ion lines.* This is no doubt because, as theoretical calculations indicate (Griem and Shen), (Bréchet and van Regemorter (49)), straight-line trajectories should be replaced by hyperbolic trajectories in the case of lines from ions broadened by interactions with charged particles. Griem (196) has recently discussed the available experimental results, and shown that most of the disagreement with theory disappears if Coulomb effects and the broadening of the lower state are taken into account. Sobel'man (428) has examined the conditions in which spectral line-broadening can give information on the inelastic scattering of electrons by excited atoms.

The broadening due to charged particles of hydrogen lines in the radio-frequency region, corresponding to transitions $n \rightarrow n + 1$, has recently been treated by Griem (196b). Here most of the broadening is due to inelastic collisions with electrons, since ion and elastic collision electron broadening are reduced because of cancellation between the upper and lower states of the transition. The calculations are consistent with observations of such lines from H II regions.

Broadening due to interactions between the radiating atom and neutral atoms is much less well understood in detail than that due to charged particles. If the interaction between the radiating and perturbing atoms can be described by an inverse power potential $V(r) = C_p/r^p$ then, for a given $p > 3$, the Lindholm-Foley theory predicts a definite value for the ratio of broadening to shift for the spectral lines, provided that the impact approximation is valid. It is often assumed that the forces between different atoms are dispersion forces, $p = 6$, but a casual glance at experimental results (see, for example, Ch'en, and Takeo) shows that the ratio, broadening : shift, is far from constant. This is partly because many of the experiments have been carried out at pressures so high that the impact approximation is unlikely to give a good description of the line profile. It is emphasized that only results obtained at sufficiently low densities of the perturbing atom can be used for comparison purposes. The actual condition is that the profile should be encompassed in a wave-number range $\Delta\nu \ll \frac{1}{2\pi c} (v^p/C_p)^{1/p-1}$

where v is the mean relative velocity of radiating and perturbing atoms; this means $N \lesssim 10^{19} \text{ cm}^{-3}$ in most laboratory experiments. Most astrophysical conditions are such that the impact approximation for neutral atom broadening is valid. Even when only low-pressure results are considered, the ratio of broadening to shift does not have an even approximately constant value. The most probable explanation is that the interaction between neutral atoms must include a short-range repulsive term, so that the whole interaction is described by, possibly, the Lennard-Jones potential $V(r) = C_{12}/r^{12} - C_6/r^6$. The profile is always Lorentzian in the impact approximation, but the measured values of broadening and shift can be used to derive values of C_{12} and C_6 . (Hindmarsh (217), Behmenberg (30), G. Smith, Hindmarsh, Petford and Smith.) The values of C_6 obtained in this way agree reasonably well (to within a factor of 2 in most cases) with calculated values, and the values of C_{12} show regularities which may also make possible the development of simple theoretical calculations for them. Most of these measurements have been made with rare gases used as the broadening agent, while in stellar atmospheres atomic hydrogen is the most important neutral broadener.

*See Addendum on page 266.

It is impossible at present to deduce within any certainty the short-range interaction for hydrogen from measures of the interaction for rare gases. A crucial experiment, not yet carried out, would be the laboratory measurement of the collision broadening and shift of a spectral line of astrophysical importance, by atomic hydrogen at low enough densities to be certain of the validity of the impact approximation. The measurements of Kusch, who used a water-stabilized arc, do not come into this category.

Much attention has recently been devoted to the 'resonance' broadening caused by collisions between atoms of the same kind. In conditions where the impact approximation is valid, theory and experiment now seem to agree to within a few per cent (Vaughan). A useful theoretical expression, which should be accurate to 10%, has been developed by Ali and Griem (5).

It is emphasized that all experiments for the determination of line profiles are very difficult; they must always be critically examined before the results are used for the interpretation of astrophysical data.

ATOMIC COLLISION CROSS SECTIONS

(Committee 2b)

The Sub-Committee on Cross Sections organized a Colloquium held at JILA in Boulder, Colorado, on 11–15 July, 1966. Here, four main topics were discussed by experts in each field: The Physics of Atomic Collision Processes; Line Broadening and Photon Scattering; Ionization and Recombination, and Data Centers; Astrophysical Problems Requiring Atomic Collision Data.

Plans for publishing the proceedings were discussed. Some review articles may be found in the *Reviews of Modern Physics* and others in JILA Reports. A review on atomic processes in stellar atmospheres prepared by B. E. J. Pagel (365) is of special interest to astrophysicists.

ATOMIC COLLISION CROSS SECTIONS

M. J. Seaton

The present report has been prepared by a group whose assistance is gratefully acknowledged: Branscomb, Burgess, Dalgarno, Hindmarsh, Van Regemorter, Bely and Geltman. The subject is a large and rapidly growing one. Only the more recent references are listed. A number of earlier ones can be found in general review papers and in the 1964 IAU Report for Commission 14.

I. General Review

Recently published books include a third much enlarged edition of the well-known text book by Mott and Massey on *The Theory of Atomic Collisions* (331); a book on the physics of atomic collisions in which the emphasis is mainly experimental (207); an introduction to atomic collision phenomena in ionized gases (306); and a book on the theory of electron-atom collisions (127). Review articles and contributed papers are published in two conference reports (194, 307), and a new review journal has been started (21). A number of reviews are being published by the JILA Data Center; these are concerned with experimental (252) and theoretical (407) work on electron impact ionization (not discussed further in the present report), and work on electron impact excitation (320). Two reviews have been published on resonance phenomena in electron collisions (65, 427). The Riga group have published collected papers on collision theory (465, 467) and a review of recent work on electron-atom collisions by Ya Veldre and Peterkop (21).

II. Data Centers

A service of systematic collection and assessment of atomic collision data is provided by two Data Centers:

1. The Information Center of the Joint Institute for Laboratory Astrophysics maintains a complete collection of papers reporting measurements or calculations of low energy (≤ 10 keV) electron collision cross sections for atoms and astrophysically interesting molecules. Several reports have been published (250, 251, 252, 320, 407, 465). A similar programme is under way for photo-ionization. Further information about the Center can be obtained from Dr L. J. Kieffer, Information Center, Joint Institute for Laboratory Astrophysics, University of Colorado, Boulder, Colorado 80302, U.S.A.

2. The Atomic and Molecular Processes Information Center, Oak Ridge National Laboratory, provides a service of collecting, storing, evaluating and disseminating information, with particular reference to work concerned with heavy particle collisions, particle interactions with electric and magnetic fields, and particle penetration into matter. Several reports have been published (346, 347, 348) and further information may be obtained from Dr C. F. Barnett, Director, Atomic and Molecular Processes Information Center, Oak Ridge National Laboratory, Post Office Box Y, Oak Ridge, Tennessee 37831, U.S.A.

III. *Electron Collisions*

(a) *Collisions with neutral atoms.* Although the energy of the He atom can be calculated to 7 significant figures, and phases for $e - \text{H}$ elastic scattering can be calculated to 3 or 4 figures, very considerable effort is required in order to calculate cross sections for near threshold electron impact excitation of neutral atoms to an accuracy much better than a factor of two (67). It is clear that the development of new methods of making such calculations is much to be desired. On the experimental side, developments in atomic beam and electron energy selection techniques have resulted in advances in the study of low energy inelastic scattering processes, and of resonances in elastic scattering, but much more could be done in obtaining reliable absolute cross section data.

There has been a great deal of interest in experimental and theoretical studies of elastic scattering resonances (see the review articles (65, 427)). Since the resonances have widths < 0.1 eV, they will generally not be of importance for electron scattering phenomena in astrophysics, for which the electron energy spread is much greater than 0.1 eV. The associated radiative processes of photon absorption in diffuse auto-ionization lines, and of dielectronic recombination, are of much greater astrophysical interest.

Calculations of elastic scattering cross sections have been made by using the method of polarized orbitals (169, 401, 439) and calculations for the alkalis have been made by Karule and others by the method of eigenfunction expansions (465). An elaborate study of elastic scattering in C, N and O and of excitation of the ground configuration terms has been made by Smith, Henry and Burke.

It is predicted by theory (167) that, due to the degeneracy of all hydrogen states with the same principal quantum number n , $e - \text{H}$ inelastic cross sections will have an oscillatory behavior in the near threshold region and will remain finite at threshold. This has been confirmed experimentally for $1s - 2s$ and $1s - 2p$ transitions in H (80, 194).

Systematic experimental studies have been made of excitation functions of observable lines in Na and K (490, 491) and a number of excitation functions of He have been measured (219, 309). Further experiments have been performed on the polarization of electron impact radiation (194, 200): for the alkalis there is good agreement with theory (194) but in a number of other cases the polarization is found to vary rapidly in the near threshold region, and further theoretical clarification is required.

(b) *Approximate formulae.* The Born approximation gives useful results for transitions in which exchange is unimportant, and is exact in the limit of high energies. A number of new calculations have been made for H (359, 468) and He (161, 276).

By using measured electron angular distributions at high energies, it is possible to deduce Born approximation cross sections for all values of the energy and, on extrapolating the data, to obtain optical oscillator strengths (277, 281, 423).

The Born-Oppenheimer approximation gives poor results for exchange processes, and attempts have been made to obtain alternative simple approximations for exchange scattering (3). One approach is to impose certain orthogonality conditions on the wave functions; this has been applied to various transitions in H and He (31, 32, 33). An approximation first proposed by Ochkur (350) consists essentially of retaining only the leading term in the expansion of the exchange amplitude in inverse powers of the energy (351, 405). Extensive calculations for excitation of H (406) and for excitation of He from the ground state (352) and from the 2^3S state (353) show good agreement with experiment at high and moderate energies. Another simple alternative to the Born and Oppenheimer approximations is to use a wave function in which allowance is made for the electron-electron interaction (460, 461). The method gives good agreement with experiment for excitation of H (104, 360).

Extensive developments have been made in the use of classical theory for the calculation of electron impact excitation and ionization cross sections. In most of this work exact classical expressions are used for binary electron-electron collisions, and various assumptions are made concerning the relative velocities of the impinging and atomic electrons (61, 255, 256, 349, 433, 474). In addition to this work on approximate classical theories, some work has been done by Percival on the exact solution of the classical problem corresponding to electron impact ionization of H. It is important to realize that classical theories can be used for electron exchange processes (61, 349). Extensive tabulations have been made for classical approximations to cross sections in N, O, Ne, Ar, Xe and Kr (466).

In semi-classical impact parameter theories, similar to the Bethe approximation, classical orbits are used for the colliding electron, and the probability of an atomic transition is calculated by using quantum perturbation theory. Such theories are superior to classical binary encounter theory at high energies (257, 416). Burgess (61) used a combination of binary encounter theory and semi-classical impact parameter theory.

Approximate formulae for allowed transitions, in which the cross section is taken to be proportional to the oscillator strength multiplied by an empirical factor \bar{g} , can give useful estimates but may be in error by factors of 2 or 3. Some improvement should result from using a form of the Bethe approximation involving a cut-off in the impact parameter (61). When formulated in such a way that conservation conditions are satisfied, this method should give reasonable cross sections for transitions with strong coupling, such as $n \rightarrow n \pm 1$ transitions in H (258, 412).

(c) *Excitation of positive ions.* The \bar{g} formula may be used for approximate estimates but may give cross sections in error by as much as a factor of 2 or 3 (66). Modified classical and semi-classical impact parameter-methods may also be used for positive ion excitation (61). Quantum mechanical calculations are generally more accurate for positive ions than for neutrals. The following methods may be used:

- (i) The Coulomb-Born (CB) approximation uses Coulomb waves in place of plane waves.
- (ii) The Close Coupling (CC) approximation requires the solution of coupled integro-differential equations.
- (iii) The Coulomb-Exchange (CE) approximation (35) is similar to the approximation of Ochkur (350, 405) for exchange excitation of neutrals.
- (iv) A number of improvements have been made in the Distorted Wave (DW) approximation (42).
- (v) The Exact Resonance (ER) approximation is used for transitions between states of the same configuration (42).

(vi) In the Quantum Defect (QD) method, information obtained from observed energy levels is extrapolated to positive energies, and used to calculate cross sections (421).

Table 9 gives a summary of calculations for electron impact excitation of positive ions. Further references are given in a previous report (420).

Table 9. Calculations for electron impact excitation of positive ions

(see also (420))

Individual Ions

Ion	States	Approximation	Reference
He ⁺	1s, 2s, 2p	CC	64, 305
Li ⁺	1 ¹ S, 2 ¹ S	CB	445
N ⁺	2s, 2p, 3s, 3p, 3d	CB, CC	66
O ⁵⁺	2s, 2p, 3p, 4p		463
Fe ¹⁵⁺	3s, 3p	CB	269
Fe ⁷⁺	3d, 4s, 4p, 4f, 5s, 5f, 6s, 6f, 7f	CB	270
Fe ¹⁴⁺	3s ² ¹ S, 3s 3p ¹ P, 3s 3p ³ P, 3s 3d ¹ D, 3s 3d ³ D	CB	38
Fe ¹³⁺	3s ² 3p ² P and 3s 3p ² ² P, ² D, ² S	CB	380
C ⁺	2p ² P _{1/2} , ² P _{3/2}	QD	
Si ⁺	3p ² P _{1/2} , ² P _{3/2}	QD	
N ³⁺ , O ³⁺	2p ² P _{1/2} , ² P _{3/2}	QD	363
Ne ⁺	2p ² P _{1/2} , ² P _{3/2}	QD	

Isoelectronic Sequences

Sequence	Transitions	Approximation	Reference	
Li	2s-ns, 2s-np, 2s-nd	CB	36, 37	
B	2p } ² P _{1/2} - ² P _{3/2}	QD and DW	42	
F				2p ⁵
Al				3p
Cl	3p ⁵	CE	413	
C	2p ²			
Si	3p ²			
C	2p ² ³ P - ¹ D, ³ P - ¹ S, ¹ D - ¹ S	DW, ER	107	
P	3p ² ³ P - ¹ D, ³ P - ¹ S, ¹ D - ¹ S	DW		

(d) *Electron collisions with molecules.* Calculations for electron collisions with molecules are obviously more difficult than calculations for collisions with atoms. The Born approximation has been used to calculate the cross sections for dissociating transitions in H₂⁺ and H₂ (249, 372, 492), and measurements have been made for dissociation of H₂⁺ by electron impact (129). Classical methods have been used to calculate excitation cross sections in heavier molecules (26). Elastic scattering by H₂ has been considered in connection with the problem of calculating the free-free absorption coefficient of H₂⁻ (431).

Inelastic differential cross sections have been measured for O₂, CO and N₂ (278, 279, 280): oscillator strengths can be obtained from extrapolation of the data. Beam measurements have been made of total cross sections in H₂, O₂ and N₂ (2, 185) in the energy range 0.5 to 15 eV. Swarm measurements in molecular gases (136) are of importance for studies of energy loss mechanisms. Some calculations have been made of scattering lengths (286).

Resonant structure has been observed in the scattering of electrons by H₂ (184, 274) and N₂ (417), and the theory has been discussed in terms of compound negative ion states (84).

Much computational effort has been devoted to the determination of cross sections for vibrational (53, 446) and rotational (85, 109, 357, 410, 447) excitation of H_2 , N_2 and O_2 . Experimental cross sections have been obtained (396, 418) for the dissociative attachment process $e + H_2 \rightarrow H + H^-$. In this work the target H_2 is mainly in the lowest vibrational state. For the inverse process, $H + H^- \rightarrow e + H_2$, which is of astrophysical interest (365), many final vibrational states must be considered.

IV. Recombination

A recent general survey by Bates (17) may not be readily available; material cited there will, therefore, be included here.

1. *Radiative recombination* coefficients for separate hydrogenic nl states have been tabulated by Burgess (60) (for $n \leq 20$ and electron temperature 0 to ∞ , by Boardman (43) (for $n \leq 10$ and $10^3 \leq T \leq 10^6$) and by Glasco and Zirin (181) (for $n \leq 15$ and $2.5 \times 10^3 \leq T \leq 2.56 \times 10^6$).
2. The importance of *dielectronic recombination* has been discussed by Burgess (59, 62) and a simple general formula for the coefficient in low density plasmas given (63). A simple treatment given by Tucker and Gould (458) involves assumptions which are not entirely correct.
3. Electron-molecular ion *dissociative recombination* has been partially reviewed by Biondi (307). The basic mechanism suggested by Bates appears to have been confirmed by the experiments of Biondi and associates (40, 95) on Ar_2^+ and Ne_2^+ . Their experiments on He_2^+ (402) also support Bate's hypothesis, but these have been criticised by Ferguson *et al.* (153).

Experimentally determined recombination coefficients have been reported for: He_2^+ (362); N_2^+ , N_4^+ (199, 242) (in good agreement); NO^+ (198); O_2^+ (41); Ne_2^+ (95, 215, 362) (in good agreement); Ar_2^+ , Kr_2^+ , and Xe_2^+ (362); Cs_2^+ (203, 206) (not at comparable temperatures). Approximate temperature variations of the coefficients are given in (198, 199, 215). Farhat (140) claims that the temperature variation for neon may be deduced from experiments of Taylor and Herkowitz but this is disputed (452).

The situation with respect to He_2^+ is rather complicated and is partially reviewed in (153) (see also comments in (95)); the abnormally small rates observed (83, 362), which may be due to the absence of any potential curve 'crossing' in the low vibrational states, means that dissociative recombination may not be the dominant process—Ferguson *et al.* (153) suggest collisional-radiative recombination instead, while Collins (94) suggests *collisional-dissociative recombination* in which a crossing is not necessary, the transitions to a repulsive state of the neutral molecule taking place due to collision with a third body.

A perturbation theory calculation for H_2^+ has been made by Wilkins (487). His conclusion that the calculation is in excellent agreement with experiment is unjustified—the experiments provide only an upper bound and may concern H_3^+ predominantly.

4. *Collisional-radiative recombination* has been reviewed briefly by Bates (307). Calculations which take into account the plasma boundary conditions to eliminate the electron temperature as an independent variable have been carried out for decaying $He^+ - e - H$ and $He^+ - e - He$ plasmas by Bates and Kingston (20). Simple approximate theories which agree well with the more detailed calculations have been given by several authors (10, 18, 295).

Several dense plasma experiments in fair to good agreement with theory have been reported (330) on He, (4 and 206) on Cs, (99) on H, but the lower density Cs plasma measurements of Hammer and Aubrey (203) disagree with theory by a factor ~ 20 .

5. *Three-body electron-ion recombination* in which the third body is a neutral atom has been treated in an elegant energy diffusion approximation by Pitaevskii (384). Detailed statistical calculations have been made by Bates and Khare (22).

The case in which one has homopolar molecules instead of atoms has been treated by Dalidchik and Sayasov (113) by using Pitaevskii's method.

6. *Ionic recombination.* The simple classical theory of Thomson (corrected by Loeb) for three-body recombination at low densities has been refined to some extent by Natanson (who also treats high densities), Bruckner (56) and Mahan and Person (293). Contrary to Bruckner's own estimates, more detailed calculations (150) following Bruckner's model agree quite well with Thomson. Keck and Carrier (247) have carried out calculations based on ideas similar to those used by Pitaevskii (384). Detailed statistical calculations (22, 307), in principle exact at low densities, have been carried out by Bates and Moffett (23, 24). Their results agree very closely with those of Thomson.

Experimental data on three-body ion-ion recombination, and on two-body recombination by electron transfer, have been reported by Mahan and Person (292) and Carlton and Mahan (76) for a wide variety of molecules. Two-body recombination in iodine has been measured by Greaves (192). Recombination in oxygen has been measured by Jütting *et al.* (240).

v. Heavy Particle Collisions

Atom-atom collision processes are of astrophysical interest at thermal energies and at very high energies. The thermal energy phenomena require special consideration, but at high energies the Born approximation may be used. Born cross sections for atomic excitation and ionization by proton impact are comparable to, but larger than, the corresponding cross sections for electron impact at the same velocity. Excitation and ionization by heavy particles other than bare nuclei is complicated by the possibility of excitation and ionization of the incident particle. Collisions in which both incident and target particles undergo transitions may be more probable, at high energies, than transitions in which only one particle undergoes a transition. High energy neutrals are of little astrophysical interest since they are readily ionized and the reverse processes of charge transfer or electron capture are improbable (47, 300). Heavy particles other than bare nuclei can induce intercombination transitions. At high energies the valence electron of the incident heavy particle may be regarded as a free electron: calculations have been made by Bates and Crothers (25) for $H + He(1^1S) \rightarrow H + He(2^3S)$.

Reviews of heavy particle collision phenomena have been given by Bates and by Wilets and Gallaher (307).

(a) High Energy Collisions.

H^+ and H incident on H and He are of particular astrophysical interest. The Born approximation is generally used, but more refined calculations are of interest in assessing its accuracy and range of validity (19, 86, 93, 163, 226, 289, 486).

Excitation of H by H^+ . Born calculations have been made for $H^+ + H(1s) \rightarrow H^+ + H(2s, 2p, 3s, 3p, 3d)$ and for $H^+ + H \rightarrow H^+ + H^+ + e$ (see (369)). The calculations for ionization are in agreement with experiment (179) above 40 keV but at lower energies give cross sections greater than those determined experimentally. The Born cross section for $2p$ excitation is about twice the measured cross section (436) between 5 and 30 keV, but is smaller than the measured cross section below 3 keV.

Cross sections for other transitions in H produced by H^+ impact may be deduced from electron impact data (74). A simple formula has been obtained (303) for excitation from the ground state to any level with large principal quantum number n . The total cross section for excitation of all discrete states has also been obtained (71). Cross sections have been calculated for $H^+ + H(n) \rightarrow H^+ + H(n')$, $n = 2, 3, 4, 5$ and 10 and $n - n' = 1$ or 2: as n increases proton impact for such transitions becomes more important than electron impact (74).

Excitation and ionization of H by H. Cross sections have been calculated by Bates and others for the excitation processes $H(1s) + H(1s) \rightarrow H(n_1l_1) + H(n_2l_2)$ and for the ionization processes $H(1s) + H(1s) \rightarrow H(n_1l_1) + H^+ + e$ or $H^+ + e + H^+ + e$ (303) and useful formula have been obtained for high energy cross sections summed over various final states.

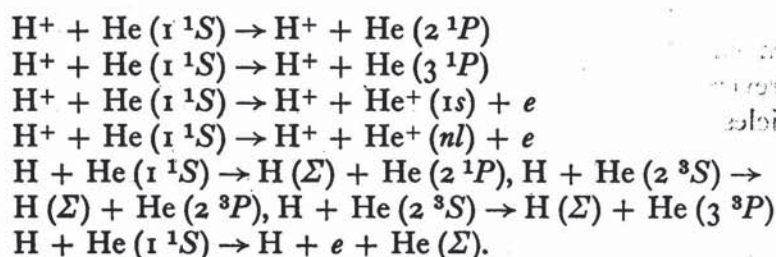
Calculations have been made of velocity distribution of electrons produced in ionization of target atoms and projectile atoms. Studies have been made of collisions for which the target atom is in an excited state (45) and for which both projectile and target atoms are in excited states (387). The charge transfer process, $H + H \rightarrow H^+ + H^-$, has also been investigated (299).

Charge transfer of H^+ in H. Cross sections for electron capture, $H^+ + H(1s) \rightarrow H(nl) + H^+$, have been computed by Bates and Dalgarno by using the Brinkman-Kramers form of the Born approximation for states up to $4f$, and this work has been extended to higher final states and to capture from excited atoms (70, 218, 302, 304). The absolute accuracy is open to question but relative values for capture into different excited states appear to be satisfactory (218). Numerous comparisons of different first-order approximations have been made.

Stopping power of H^+ in H and of H^+ in an H^+ , e plasma. The efficiency with which a beam of protons is slowed down in a gas of ground state hydrogen atoms has been examined in detail and the mean energy expended in producing an ion pair has been calculated by Dalgarno and others.

The energy loss of fast protons in an H^+ , e plasma has also been calculated; the presence of free electrons produces a marked increase in the loss rate.

Excitation and ionization of He by H^+ and H. Calculations for excitation and ionization are much less extensive for He than for H. The following processes taken mostly from earlier work have been studied:



Σ here denotes a sum over all final states.

The calculated ionization cross sections agree with measured cross sections at energies above 400 keV, but are larger than measured cross sections at lower energies. These results are prior to 1963 and individual references are not included.

Charge transfer of H^+ in He. The Born approximation has been used (298) to calculate cross sections for $H^+ + He(1^1S) \rightarrow H(nl) + He^+(n'l')$. The calculated total charge transfer cross section agrees with experiment above 40 keV, and the calculated cross section for capture into the $3s$ state of H agrees with experiment (224) above 100 keV but is greater than the experimental cross section at lower energies. Experimental evidence (224) suggests that the cross section for capture into the n th state of H varies as n^{-3} for impact energies above 20 keV. At energies below 20 keV, the calculated cross sections for capture into $H(2s)$ and $H(2p)$ are considerably larger than measured values (see (227, 307, p. 618)).

The capture process for the case of H and He^+ in their ground states has been studied by using higher order approximations (46, 48, 193).

(b) Low Energy Collisions.

Excitation by proton impact. Cross sections for excitation by electron impact and by proton impact are broadly similar as functions of the velocity of the electron or the proton. For the

electron case, cross sections rise rapidly from threshold to a maximum which occurs at a velocity corresponding to about twice the threshold energy, ΔE ; the cross sections then decrease asymptotically as $E^{-1} \ln E$ for optically allowed transitions or E^{-1} for optically forbidden transitions. It follows that, in thermal conditions, proton impact will be more important than electron impact only if $kT \gg \Delta E$. A process for which this condition is satisfied is $H^+ + H(2s\frac{1}{2}) \rightarrow H^+ + H(2p\frac{1}{2}, 2p\frac{3}{2})$. The corresponding charge transfer process, $H^+ + H(2s\frac{1}{2}) \rightarrow H(2p\frac{1}{2}, 2p\frac{3}{2}) + H^+$, has a much smaller cross section. Proton impact can also be of importance in redistributing angular momentum, $H^+ + H(nl) \rightarrow H^+ + H(nl \pm 1)$, for higher excited states (374). For proton collisions with positive ions the repulsive Coulomb field reduces the cross sections, but under coronal conditions the reaction rate for $H^+ + Fe^{13+}(3p\frac{1}{2}) \rightarrow H^+ + Fe^{13+}(3p\frac{3}{2})$ is still comparable with the rate for direct excitation by electron impact (419).

The condition $kT \gg \Delta E$ can also be satisfied for transitions between molecular rotational states. Calculations have been made (453) for $H^+ + CN(\tilde{J} = 0) \rightarrow H^+ + CN(\tilde{J} = 1)$, which may be of importance in connection with the cosmic microwave radiation at $\lambda = 2.63$ mm (158). It may be expected that the cross sections for excitation of higher rotational levels will be of a similar order of magnitude.

Charge transfer. The process of symmetrical resonance charge transfer, $H^+ + H \rightarrow H + H^+$, does not involve an electronic transition and its cross section can be predicted reliably (373). The process is of importance in considering diffusion of H^+ in H.

Asymmetric charge transfer, $H^+ + X \rightarrow H + X^+$, involves an electronic transition and will, in general, proceed very slowly at thermal energies. Exceptions occur and one such is $H^+ + O(^3P) \rightarrow H + O(^4S)$, which is accidentally resonant. Cross section estimates for the reaction at thermal energies, which are of interest for astrophysical and geophysical problems, have been obtained from an analysis of experimental data at higher energies and from an analysis of upper atmosphere data.

Radiative charge transfer. Radiative charge transfer may proceed more rapidly than ordinary charge transfer at thermal energies. Calculations have been made by using a simple theory. Reactions investigated are $He^{2+} + H \rightarrow He^+ + H^+ + h\nu$ and $He^{2+} + He \rightarrow He^+ + He^+ + h\nu$ (6).

Radiative association. Calculations have been made for $H^+ + H \rightarrow H_2^+ + h\nu$, $C + H \rightarrow CH + h\nu$, $C^+ + H \rightarrow CH^+ + h\nu$ and for the free-free transition $H^+ + H \rightarrow H^+ + H + h\nu$. The rate of formation of HeH^+ has not been calculated though the molecule undoubtedly exists (205, 315).

The process $H + H + h\nu \rightarrow H_2'$, free-bound absorption, has been investigated by Solomon and others (429) for the transition $1s\sigma 2p\sigma^3\Sigma_u^+ \rightarrow 1s\sigma 2s\sigma^3\Sigma_g^+$, and does not appear to be an astrophysically important source of opacity.

Radiative association of two hydrogen atoms, $H + H \rightarrow H_2 + h\nu$, has a very small rate coefficient (297).

Collision-induced radiative deactivation. Because of the large polarizability of He (2^1S), the reaction $H^+ + He(2^1S) \rightarrow H^+ + He(1^1S) + h\nu$ proceeds quite rapidly. A similar study has been made for $He(1^1S) + He(2^1S) \rightarrow He(1^1S) + He(1^1S) + h\nu$ (7).

Associative detachment. Reactions of the type $X + Y^- \rightarrow XY + e$ provide efficient mechanisms for the removal of negative ions. A simple model for $H + H^- \rightarrow H_2 + e$ suggests a rate coefficient of $10^{-10} \text{ cm}^3 \text{ s}^{-1}$. Developments in the theory of resonating states should yield a more precise estimate. The process is of importance in connection with the H^- abundance in stellar atmospheres (365) and in that it provides a mechanism for the formation of H_2 .

Mutual neutralization. Reactions of the type $X^+ + Y^- \rightarrow X + Y$ usually proceed rapidly. The case of $H^+ + H^- \rightarrow H + H$ has been studied in detail.

Penning ionization. Processes of the type $X^* + Y \rightarrow X + Y^+ + e$ can also occur with high

efficiency. Rate coefficients for $\text{He}(2^1\text{S}) + \text{H} \rightarrow \text{He}(1^1\text{S}) + \text{H}^+ + e$ and $\text{He}(2^3\text{S}) + \text{H} \rightarrow \text{He}(1^1\text{S}) + \text{H}^+ + e$ may be of the order $10^{-11} \text{ cm}^3 \text{ s}^{-1}$. Much larger values may occur, especially when a pair of excited atoms is involved.

Excitation of rotation of H_2 by H impact. Calculations have been made of the rate coefficients for $\text{H} + \text{H}_2(\mathcal{J} = 0) \rightarrow \text{H} + \text{H}_2(\mathcal{J} = 2)$, which is of importance for the cooling of the interstellar gas. Further refinements (8, 112) give reaction rates which are in good general agreement with the earlier work but somewhat smaller at the higher temperatures considered. The main uncertainty is in the $\text{H} - \text{H}_2$ interaction potential. Rate coefficients have also been obtained for other rotational transitions in H_2 and D_2 (112), and for $0 \rightarrow 1$ rotational transitions in CH , CN and OH produced by H atoms.

Calculations have been made for $\text{H}_2(\mathcal{J} = 0) + \text{H}_2(\mathcal{J} = 0) \rightarrow \text{H}_2(\mathcal{J}) + \text{H}_2(\mathcal{J}')$ (115).

Transitions between fine and hyperfine structure levels by H atom impact. Calculations have been made (108), in varying degrees of refinement, of the reaction rate for $\text{H} + \text{H}(F = 0) \rightarrow \text{H} + \text{H}(F = 1)$, which is of importance for 21 cm studies.

The processes $\text{H} + \text{O}(^3\text{P}_j) \rightarrow \text{H} + \text{O}(^3\text{P}_{j'})$ and $\text{H} + \text{C}^+(^2\text{P}_j) \rightarrow \text{H} + \text{C}^+(^2\text{P}_{j'})$ and $\text{H} + \text{Si}^+(^2\text{P}_j) \rightarrow \text{H} + \text{Si}^+(^2\text{P}_{j'})$ contribute to the cooling mechanism in the interstellar gas. Recent work (426) suggests that the $\text{H} + \text{O}$ reaction may be the most important, but the theory used was one developed for the study of collision-induced changes in hyperfine structure (111) and may not be adequate for changes in fine structure (73, 342).

Quenching collisions. Reactions of the type $\text{X} + \text{Na}(^2\text{P}_{1/2}) \rightarrow \text{X} + \text{Na}(^2\text{S}_{1/2})$ have been studied theoretically (341) but the lack of adequate wave functions for the quasi-molecule XNa has prevented quantitative predictions. Experimental results are available for the case in which X is an inert gas (435). Further study of the case for which X is atomic hydrogen may be of importance for work on the formation of strong lines (365).

Chemical reactions. Exothermic reactions which produce H_2 and CH , OH , NH , CN , CO and N_2 have been discussed. It is conventional practice to express the rate coefficient in Arrhenius form.

Transport properties. The thermal conductivity and viscosity of atomic hydrogen have been calculated to high accuracy at high temperatures and low temperatures (57). Formulae are available for the transport coefficients of fully ionized plasmas (116).

Ion-molecule reactions. New laboratory techniques have been developed for the study of reactions of ground state atomic and molecular ions (positive and negative) with neutral species, including unstable species such as O , N and O_3 (148). Measurements are made at 300°K . Results have been obtained for a large number of reaction rates which are of interest for studies of the upper atmospheres of the Earth (154, 155) and of Mars (345) and of processes in comet tails (148). It is found that exothermic charge transfer to molecules is generally fast. In the case of negative ions, many fast associative detachment reactions are found to occur (149).

A comprehensive survey and review is being prepared (78).

MOLECULAR SPECTRA

(Committee 3)

J. G. Phillips

For the sake of brevity, this report will be limited to progress in the study of those molecules that are of immediate interest to astrophysicists. This means that the main emphasis will be on certain diatomic molecules, though a few of the simpler polyatomic molecules will have to be included. Even with this limitation a reasonably complete bibliography of papers that have appeared since the Hamburg meeting would include over 220 titles. Not all of these are listed here; instead, the emphasis will be on papers summarizing information on the various molecules.

Before turning to the individual studies, it might be worth mentioning that a complete card file bibliography is maintained at Berkeley, and inquiries are welcome. In addition, a bi-monthly Newsletter is distributed from Berkeley in collaboration with S. P. Davis of the Physics Department. This Newsletter includes information on work currently in progress at various laboratories.

1. Analyses and Molecular Constants

N_2 . Several investigations of the nitrogen spectrum in the vacuum ultraviolet have been carried out. Tilford, Vanderslice, Wilkinson and others at NRL have observed the absorption spectrum between 1060 and 1520 Å (455). In addition, the vacuum ultraviolet nitrogen afterglow has been described by Tanaka *et al.* (448), and Codling has investigated the structure in the photo-ionization continuum of N_2 near 500 Å (90). Miller has described some high-resolution Vegard-Kaplan bands observed in emission (317). Isotope shifts have been observed by Mahan-Smith and Carroll in some weaker systems (294), while Ogawa *et al.* have studied isotope shifts in the vacuum ultraviolet (354). As far as theoretical calculations are concerned, Rydberg levels have been calculated by Lefebvre-Brion and Moser (285). Sahni and De Lorenzo have carried out self-consistent field calculations of the ground, ionized, and excited states of both N_2 and O_2 (409).

CN. The rotational and vibrational constants of the Red System are being re-evaluated by Rigutti and Poletto at Arcetri; Fishburne and others at Ohio State University have extended the observation of the Red System beyond 1 μ . The results of the latter are to be published in the *J. molec. Spectrosc.* Published studies include one by Radford on the hyperfine structure of the $B^2\Sigma^+$ state (390), and a report by Evenson *et al.* on the optical detection of microwave transitions between excited electronic states and the identification of the transitions involved (138). By using high resolution solar spectra obtained at the Jungfraujoch by Delbouille and Roland, Benedict has identified about 2860 lines between 7498 and 12 016 Å as being due entirely or partly to solar CN. With the aid of these observations, it has been possible to complete the laboratory work by Phillips concerning this molecule.

H_2 , HD, D_2 . An important series on the absorption spectra of these molecules is being published by Monfils (321). General studies of electronic excited states of H_2 have been carried out by Browne (54), Rothenberg and Davidson (404), and Wakefield and Davidson (475). The absorption spectrum in the vacuum ultraviolet is being investigated by Namioka (332); the infrared spectra of hydrogen and helium have been described by Gloerson and Kieke (183). Calculations of fine structure constants of metastable H_2 in the $C^3\Pi_u$ state have been carried out by Chiu (87); Ross and Phillipson have calculated force constants for both H_2 and H_2^+ (403). A molecular orbital description of the lowest excited singlet state of H_2 has been published by Kato *et al.* (243). Wave-functions for H_2 and H_2^+ have been calculated by Goodisman (186).

He_2 . Of primary importance is a series of articles by Ginter on the spectrum and structure of this molecule (180). In addition, Browne has studied some excited states of the helium molecule (55).

C_2 . (See also p. 250). The electronic structure of C_2 has been described by Fougere and Nesbet (160). Some new bands in the Swan system of C_2 have been reported by Bugrim and his co-workers (58). Solomon and Stein have studied the infrared absorption of C_2 , as well as CO and CN (430). The analysis of 35 bands of the Swan system of C_2 has been completed at Berkeley, and is being published by the University of California Press.

Hydrides and Deuterides. Milligan and Jacox have reported on the infrared spectrum of NH as produced in the photolysis of NH_3 in inert and reactive matrices (318). A rotational

extension of the ($c^1\Pi - a^1\Delta$) system of NH and ND has been published by Shimauchi (422). Asundi writes that the Spectroscopy Division, Atomic Energy Establishment, Trombay, has submitted for publication an analysis of the (0 - 1) and (1 - 1) bands of the ($d^1\Sigma - c^1\Pi$) system of NH, and has completed the rotational analysis of the (0 - 0) band of the ($A^3\Pi - X^3\Sigma$) system of ND.

The OH radical has been studied in the infrared and vacuum ultraviolet by Ogilvie (356) and Felenbok and Czarny (151), respectively. The latter identified the ($C^2\Sigma - X^2\Pi$) system of OH and OD. Finally, the observation of a sequence in the ($A^2\Sigma - X^2\Pi$) system of OH has been reported by Stoebner *et al.* (438).

The recent interest in discrete lines in the radio spectrum of interstellar matter has resulted in laboratory and theoretical investigations of the radio frequency lines of CH by Douglas and Elliott (123) and Goss (188).

The analysis of a CaH band at 2883 Å and CaD bands at 2720 Å, 2789 Å and 2877 Å has been published by Khan (248).

Oxides. The past two years have seen the appearance of many studies of the spectrum of NO. Of fundamental importance is a series by Miescher and various collaborators (126, 237, 275, 316). Horn and Dickey have reported on the near-infrared emission spectrum of NO (220); observations in the same region have led to the calculation of molecular constants of NO by Olman *et al.* (358). Rydberg series in the NO spectrum have been investigated by Lefebvre-Brion and Moser (284) and by Huber (221). Representative of papers on the rotation-vibration spectrum of NO are reports by Meyer and Haeusler (313), Aubel and Hause (13) and Meyer *et al.* (314).

Krupenie of NBS has published a review entitled *The Band Spectrum of Carbon Monoxide* (272). It includes a description of CO, CO⁺, and CO⁺⁺. He is, also, preparing a review on the spectrum of molecular oxygen. Also of importance are molecular constants derived by Rank *et al.* for CO by using a heated absorption tube in the infrared (394). Other studies of the CO infrared spectrum include work by Weinberg *et al.* on a hot band at 4.7 μ (478), and by Solomon and Stein (430). At the extreme end of the spectrum, we have a report on the radio-frequency spectrum of the $a^3\Pi$ state of CO by Freund and Klemperer (162). The high resolution vacuum ultraviolet spectrum has been investigated by Tilford *et al.* (454). The rotational structure of the $d^3\Delta$ state of CO has been examined by Kovacs (267).

Most of the work that has appeared on the O₂ molecule has involved the ultraviolet. The absorption spectrum in the extreme ultraviolet has been described by de Reclhac and Damany-Astoin (398). Codling and Madden have discovered a new Rydberg series near 500 Å (89). Self-consistent field calculations of O₂ have already been mentioned above in connection with N₂ (409).

Several metallic oxides have been studied during the past two years. Becart and Mahieu have discovered new heads in the visible system of AlO (29). Asundi reports the discovery of a new band system of AlO in the region 2300-2800 Å, by the group at Trombay. Weltner and McLeod have identified the ground state of ZrO from neon matrix investigations at 4°K (479). The ultraviolet spectrum of MgO has been studied by Pesic and Kliska (379). Kasai and Weltner have investigated the ground states and hyperfine-structure separations of ScO, YO, and LaO (241). Dunn (Michigan) and Klemperer (Harvard) have reanalyzed the LaO and ScO spectra in order to resolve the question of the doublet or quartet structure of the ground state. Their results show that the ground state is $^3\Sigma$. In the case of TiO, Kovacs has carried out a thorough investigation of the triplet terms (268), and Toros has studied the anomalous multiplet splitting of these triplet terms (457). Asundi writes that the group at Trombay has carried out vibrational and rotational analyses of five bands of the orange system of FeO.

Molecular Ions. Stuart and Matsen have calculated a one-center wave function for the ground state of the HeH^+ molecular ion (440). H_2^+ force constants have been calculated by Ross and Phillipson (403), while Peek has calculated eigen parameters for certain orbitals of H_2^+ (371), and Wind has investigated vibrational states of that same ion (488). A study of the electronic structure of CH^+ has been made by Morre *et al.* (327). For CO^+ , publications include that of Krupenie and Weissman on potential energy curves (271) and of Ogawa describing a Rydberg series in CO converging to the $B^2\Sigma^+$ state of CO^+ (61). Two papers have appeared on the C-X system of N_2^+ as the result of work by Joshi (235). Finally, Asundi writes that a reinvestigation of the rotational structure of the bands of the second negative system of O_2^+ in the 2100–6100 Å region is in progress at Trombay.

Polyatomic Molecules. A description of the near infrared spectrum of water and aqueous solutions has been published by Yamatera *et al.* (489). Bayly *et al.* have carried out a study of the absorption spectra of liquid phase H_2O , HDO and D_2O from 0.7 to 10 μ (28). At the other end of the spectrum, Bell has investigated the spectra of H_2O and D_2O in the vacuum ultraviolet (34). An important analysis of the 4050 Å group of the C_3 molecule has been made by Gausset *et al.* (177), see p. 250. Several publications have appeared on various aspects of the infrared spectrum of CO_2 ; examples are a description of the 2.8 μ bands by Gordon and McCubbin (187), of the 4.3 μ bands by Rao and Oberly (395), and a new measure of the 3 ν_3 band by Fayt *et al.* (147). Dixon has shown that the CO flame bands represent transitions from the lowest excited state of CO_2 , 1B_2 to the ground state (117a).

Herzberg and his colleagues at the National Research Council of Canada are actively engaged in studying the spectra and structures of diatomic molecules, simple polyatomic molecules and free radicals. A brief summary of work on selected molecular spectra under investigation, prepared by Herzberg, is presented below.

C_2 . It has been established by Ballik and Ramsay (15) that the ground state of the C_2 molecule is not the lower state of the Swan bands (3I_u) but the lower state of the Mulliken bands ($^1\Sigma_g^+$), and the energy difference between these two states is 610 cm^{-1} . Several other new electronic states have been found and their constants have been determined. Herzberg has recently found a simple new band system which represents a $\Sigma_u^+ - \Sigma^+$ transition of C_2 or C_2^+ or C_2^- (214). Neither the upper nor lower state has been observed previously.

Absorption Spectra, Diatomic Molecules: Si_2 , P_2 , BH, SiH, NF, NCl. The spectrum of Si_2 has been studied by Verma and Warsop (469) and that of P_2 by Creutzberg (103). In both cases a number of new electronic states have been found.

Several investigations on diatomic hydrides have been made in the near and far ultraviolet regions. Bauer *et al.* (27) have made a detailed study of the absorption spectrum of BH, and additional results on this molecule have been obtained by Johns *et al.* (233). Two new systems of SiH and SiD have been found and analyzed by Verma (470). The spectrum of HS has been studied by Morrow (328).

Until recently no spectroscopic information about the molecules NF and NCl has been available. Douglas *et al.* (125) have now observed very simple and interesting spectra of these molecules which are analogues of the visible and infrared absorption bands of the O_2 molecule.

Polyatomic Molecules and Radicals: CH_2 , BH_2 , PH_2 , AlH_2 , SiH_2 , HCP, HCO, HCF, HCCl, HSiCl, HSiBr, C_3 , NO_2 , CS_2 , CF_2 , NH_3 , CH_4 .

The investigation of the red bands of CH_2 has been completed (213) and a similar spectrum has been found for the BH_2 radical, which is new (213). Dixon *et al.* (117) have succeeded in analyzing one of the bands of PH_2 originally discovered by Ramsay (392), and they have established the structure of the molecule in the upper and lower state. Spectra of AlH_2 and SiH_2 have also been obtained, but the analyses are not yet complete.

The HCP molecule (an analogue of HCN) has been studied by Johns *et al.* (234) and the absorption spectrum of HCO has been further studied by Johns *et al.* (232).

Phillips has referred to the extensive analyses of the 4050 Å group of the C₃ radical, based on new absorption spectra obtained by the flash photolysis technique (177). The electronic transition has been definitely identified as $^1\Pi_u - ^1\Sigma_g^+$, and improved molecular constants have been determined. Extensive spectra of the two isomeric molecules CCN and CNC have been obtained and studied by Merer and Travis (311), and fairly complete analyses of the spectra of NCN and N₃ have been completed by Herzberg and Travis (211) and Douglas and Jones (124).

A new study of NO₂ in the visible region has been made by Douglas and Huber (122). One progression of simple bands has been found, but the remainder of the spectrum is extremely difficult to analyze because of the presence of innumerable perturbations. This spectrum is of particular astrophysical interest because of the suggested possibility of its presence in Mars (253).

The near ultraviolet spectrum of CS₂ has been reinvestigated by Kleman (260), Douglas and Milton (120), and Douglas and Zanon (121).

Douglas has continued work on the spectra of NH₃ in the vacuum ultraviolet (119). The infrared and Raman spectra of CH₄ have been studied by Herranz and others (209, 210).

Other molecular spectra are also on the Ottawa program but they are less likely to be of astrophysical interest than those mentioned above.

Mme R. Herman and her collaborators at Meudon report the following:

Mg₂—Bands observed at high temperature near 2852 Å (296, 480).

Al₂, AlH—Diffuse bands observed near 2700 Å (481).

CaH—Studies of satellites in red, and pressure effects (482).

C₂—Absorption spectra observed in an electric discharge source reveal short lifetimes (208).

At the Dominion Astrophysical Observatory, Wright reports some work on diatomic molecules of astrophysical interest. Tatum and Nichols are preparing papers on two subjects: one on 'Partition Functions and Association Equilibria' (450) and one on 'Intensity Data' (449).

II. Intensities and Transition Probabilities

J. G. Phillips

N₂, N₂⁺. The following are representative of the numerous investigations that either have been or are in the process of being carried out on the nitrogen spectra: (a) An extensive series of studies at the University of Maryland and NRL by Benesch *et al.* (39); (b) the use of an electron beam excitation by Jeunehomme to study the oscillator strengths of the first negative and second positive systems (230); (c) the observation of the intensity distribution of the Lyman-Birge-Hopfield band system by McEwen and Nicholls (308), and the calculation by Nicholls of Franck-Condon factors for the Gaydon-Green band system (339); (d) an excellent calculation of Franck-Condon factors by Zare *et al.* (493); (e) a recent determination of vibrational transition probabilities and *r* centroids for the C-X system by Joshi (236).

CN. The oscillator strength of the CN red system has been investigated by Jeunehomme (229). Other studies of the red system include the observation of the radiative lifetime of the $^3\Pi$ state by Wentink *et al.* (483) and an interesting derivation of *f*-values for the red system from the solar spectrum by Poletto and Rigutti (386). Reis has investigated the oscillator strength of the violet system (400), while Kudryavtsev *et al.* have determined the matrix element of the dipole moment for the electronic transition of the violet system (273).

H₂, D₂, T₂. A general description of the properties of the hydrogen molecule has been published by Dalgarno and Williams (110). Rank, Wiggins and their collaborators have

observed the intensities of hydrogen quadrupole bands, as well as intensities of features in the spectrum of H_2O and CO_2 (159, 393). A general description of transition probabilities in the electronic and vibrational spectra of the hydrogen molecule has been produced by Geiger and collaborators (178). For the ultraviolet, calculations have been made of vibrational overlap integrals by Patch (367), an experimental study of the continuum emission by Hamberger and Johnson (202), and of total absorption cross sections of H_2 , N_2 and O_2 in the 550–200 Å region by Samson and Cairns (411).

C_2 . The Swan system has been the subject of four investigations. Absolute band strengths for the Swan system have been derived by Mentall and Nicholls (310). Jain has published transition probability parameters of the Swan and the Fox-Herzberg band systems (228). In addition, shock-tubes have been used by Fairbairn (139) and by Harrington *et al.* (204), to obtain experimentally the oscillator strengths of the Swan bands. On the theoretical side, Franck-Condon factors have been calculated for the C_2 band systems by Ortenberg, as well as for band systems of NO and CO (361).

O_2 . The photo-ionization and absorption cross sections of O_2 and N_2 in the 600 to 1000 Å region have been observed by Cook and Metzger (97). In the same spectral region the absorption cross section of oxygen has been studied by Kosinskaya and Startsev (265), and Nicholls reports that he and Degen have almost completed intensity measurements on bands of the Herzberg system. Halmann and Laulich have studied the vibrational transition probabilities in the Schumann-Runge absorption bands of $^{16}O_2$ and $^{18}O_2$ (201). In the infrared, Badger *et al.* have observed the absolute intensities of the discrete and continuous absorption bands of oxygen at 1.26 and 1.065 μ , and the radiative lifetime of the $^1\Delta_g$ state (14). Finally, two recent studies of the negative band systems of O_2^+ have been published by Nicholls (340) and Jeunehomme (231).

Oxides. The absolute transition probabilities in the ultraviolet spectrum of CO have been observed by Hesser and Dressler (216), and by Cook *et al.* who observed the photo-ionization and absorption coefficients in the 600 to 1000 Å region (98). Kovacs and Toros have discussed the intensity distribution in the triplet bands of CO (266), while two recent works discuss the $A^1\Pi - X^1\Sigma^+$ system; the first is by Skerbele *et al.* on vibrational intensities (424), and the second is by Tilford and Simmons on the electric quadrupole component (456). In the infrared, Breeze and Ferriso have studied the integrated intensities of the fundamental and first overtone bands of CO between 2500° and 5000°K (52). Finally, for the ion CO^+ there is an investigation of lifetimes and transition probabilities by Lawrence (282).

The NO spectrum has been the subject of several investigations. Of general interest are (a) the experimental study of transition probabilities in the β and γ band systems by Antropov *et al.* (12), and (b) a somewhat more recent parallel study of the δ , γ and β band systems of NO by Erkovich and Ageshin (137). The effect of temperature and pressure or path length on band strengths of NO has been investigated by Carpenter and Franzosa (77) and by Churchill and Meyerott (88); the latter, in discussing the spectral absorption of heated air, also provides data on N_2 and O_2 absorption. The rotation-vibration NO spectrum has been investigated by Breeze and Ferriso, who measured the integrated intensities of the 5.3 μ fundamental and the 2.7 μ overtone bands at temperatures between 1400°K and 2400°K (51). In somewhat more detail, the widths and strengths of vibration-rotation lines in the fundamental band of NO have been measured by Abels and Shaw (1).

Relatively little has been done recently on intensities in the spectra of metallic oxides. Tawde and Korwar have studied the effective vibrational temperature as a variant of the electronic transition moment in AlO (451). Somewhat earlier there appeared a calculation of wave functions and binding energies of the TiO molecule by Carlson and Nesbet (75).

Polyatomic Molecules. Reference has already been made to the work of Rank and his co-workers on CO_2 (393). Additional publications of a general nature include the report by

Penner and Varanasi on approximate band absorption and total emissivity calculations for CO_2 (377), and the work of Gray and Selvidge on relative intensity calculations (189). Finally, several studies involve measures of intensities of specific CO_2 features: (a) of the 4.3μ band, by Gray (190), and Ferriso *et al.* (157); (b) of the 9.4μ and 10.4μ bands, by Rasool (397) and Gray (191); (c) of the 15μ band, by Varanasi and Lauer (462).

Many investigations have been carried out during the past two years on various aspects of the emission or absorption spectrum of H_2O . It was one of the molecules investigated by Metzger and Cook on continuous absorption, photo-ionizations and fluorescences in the 600 to 1000 \AA region (312). In addition to H_2O , they studied NH_3 , CH_4 , C_2H_2 , C_2H_4 , and C_2H_6 . The absorption and photo-ionization cross sections of H_2O were measured by Watanabe and Jursa (477), while the emissivity of water vapor at temperatures to 1000°K has been observed by Podkladenko (385). Penner and Varanasi have made approximate band absorption and total emissivity calculations for H_2O (378). Studies of specific bands of H_2O include one by Ferriso and Ludwig on spectral emissivities and integrated intensities of the 1.87μ , 1.38μ and 1.14μ bands between 1000°K and 2200°K (156). Patch has carried out measurements of the absolute intensity of the 2.7μ band of water vapor in a shock tube (368), and this same band has been investigated by Maclay in an observation of integrated absorptances (291). At still longer wavelengths there are observations of spectral emissivities and integrated intensities of the 6.3μ fundamental band by Ludwig *et al.* (290), and a study of the line breadth of the 1.64 mm absorption in water vapor by Rusk (408).

III. Atlases

A very useful series of identification atlases of molecular spectra is being produced by Nicholls and his co-workers. To the present time, three atlases have been published: (a) the $\text{AlO } A^2\Sigma - X^2\Sigma$ blue-green system; (b) the N_2 second positive system; (c) the N_2^+ first negative system.

Volume III of *Molecular Spectra and Molecular Structure*, by Herzberg, (212) has been completed. A revision of the Table of Molecular Constants in his book entitled *Spectra of Diatomic Molecules* is being prepared by Huber and Herzberg.

VACUUM-ULTRAVIOLET ATOMIC SPECTRA

Observations of the XUV solar spectrum and of stellar spectra (329) have stimulated renewed interest in laboratory spectra of highly-ionized atoms. R. Wilson reports on the work at Culham laboratory, as follows:

High Temperature Plasmas. These sources include a range of thetatron plasmas and the pinch discharge Zeta, supplemented by a high voltage spark. Most of the intense solar lines reported earlier in the range 170 to 220 \AA have been identified by Gabriel and Fawcett as due to Fe VIII to Fe XII, and Fe XIV (144, 145, 164, 166). Isoelectronic sequences from Ca through Ni have resulted in the identification of highly-ionized Ni in the Sun to the short-wave limit 60 \AA (165). Recent work on Fe XII, XIII, XV, XVI is leading to further solar identifications.—In the soft X-ray region from 15 to 100 \AA , newly observed spectra of Ne VII, Ne VIII, Ar IX to Ar XII, Kr IX, Kr X, Xe IX, Sc XII, Sc XIII, Ti XIII, Ti XIV, and V XIV, V XV are being investigated (141, 142, 143).—*Laser-Produced Plasmas.* The production of hot dense plasmas by focussing a high-powered laser beam on a solid target in vacuum is proving to be a very powerful source of excitation that permits a good isolation of ionization stages. Results for Fe XV and Fe XVI have been published (146), and the spectra Cr XV, Cr XVI; Mn XVI, Mn XVII; Fe XVII, Fe XVIII; Co XVIII and Co XIX are being analyzed.

The spectra of the iron-group elements in high ionization stages are being studied also at the Hebrew University, Jerusalem, by Alexander, Feldman, Fraenkel and Hoory. Their latest results concern Co VIII, Ni IX, Cu X (4a) and Cr VI, Mn VII, Fe VIII (150a).

At Lund University, L. Å. Svensson and J. O. Ekberg are using a 5 m grazing incidence spectrograph for a systematic investigation of the vacuum-spark spectra below 400 Å of elements in the iron group. The work on titanium has been completed, the result being a list of some 500 wavelengths accurate to about 0.003 Å and comprising ionization stages from Ti v to Ti xii.*

At Uppsala, Bockasten and his group have developed a small theta pinch into a highly efficient light source for intermediate stages of ionization. They have applied it to the study of N III–N VI and O III–O VI. Some preliminary results are given in (43a), and the definitive description of N IV and N V has been published by Hallin (200a, 200b). This work covers the entire region from the shortest wavelengths to the near infrared.

At NRL in Washington, Tilford reports the observation of highly-ionized spectra of N and O in the region below 400 Å, with a resolution 0.04 Å. Asymmetrical auto-ionized emission lines have been observed above the first ionization limit in N III. Multiplets of Ne IV have also been observed.

In the Far Ultraviolet Physics Section of the National Bureau of Standards, Madden, Codling and Ederer have continued their observations of atomic spectra made with synchrotron light as a background source. In the case of Ne I two basic types of transition have been found in the range 150 to 275 Å: the excitation of a subshell 2s-electron to outer p-orbits and the simultaneous excitation of two outer 2p-electrons (92). A 3-meter grazing incidence monochromator has been constructed for use with the synchrotron in the region 50 to 300 Å (131). It has been used to determine the absolute absorption cross section near selected broader resonance profiles in the photo-ionization continua of He, Ne (91) and Ar (130).

Garton reports active research in his laboratory at Imperial College. J. M. Wilson has accumulated vacuum ultraviolet absorption spectra of Si, Ge, Sn, Pb. The work on Pb I has been completed (176). Connerade has greatly extended the observations in two spectra which were originally studied by Beutler, Hg I and Cs I. He plans to reobserve Tl I and Rb I, similarly. The range is 600 to 900 Å. He is using six times the dispersion of the early work, and thus can greatly extend the series. In this region, Goldstein has found interesting series in Pb I converging on the limits sp^2 ^{2,4}L. Learner and Morris have found new autoionizing levels in Hg I from emission spectra.

In the grazing incidence region, Burgess, Jenkins, and Mansfield have used a large capacitor bank known as 'Maggi I' as a source to produce the spectra C IV and N V. Line broadening and shifts are being studied.

In collaboration with colleagues at Argonne and Harvard the principal series of Ra I have been extended to $n = 50$; and Ba I series to $n = 80$ according to Garton. Some corrections in Ca I (173, 337) have been made, and new auto-ionizing resonances in Tl I (174) and In I (366) have been observed. Important new series in La I have been published (175).

GENERAL WORK ON ATOMIC SPECTRA

At the National Bureau of Standards emphasis is being given to first and second rare-earth spectra of the lanthanon group in order to provide data for Volume IV of *Atomic Energy Levels*. A summary of this work is in print and need not be repeated here (324). Suffice to say that the first and second spectra of Ce, Pr, Pm, Ho, Tm and Yb are on the Bureau Program.

In Amsterdam, Klinkenberg and his associates are working on Nd I, Nd II, Tb I (261) and Tb II. Er I (301, 389, 432) and Er II are being studied by a number of workers.

Third and fourth spectra of this group are being investigated at The Johns Hopkins University. This program was started by the late G. H. Dieke in collaboration with Crosswhite. Third spectra may prove to be of astrophysical importance, since they have strong infrared

lines; fourth spectra may, also, be of interest. Recent analyses of La III (444), Ce III (442), Pr III (441), Pr IV (443) and Gd III (72) have been published.

Mention should be made of the program in progress at the Radiation Laboratory in Berkeley. Here, Conway and his associates have extensive observations of Dy I and Dy II. They are also progressing with the observation and analysis of spectra in the actinon group: Cm I, Cm II, Bk and Cf.

At the Laboratoires de Bellevue, Blaise has continued his work on Pu I and Pu II in collaboration with Argonne. A detailed report of all spectra on their program has been published by Chabbal and Jacquinet (79).

Prokofiev reports that series regularities in spectra have been studied experimentally; perturbations, being reflected by both transition probabilities and quantum defect, have been found in the main series of Ca I, Sr I and Ba I; in the diffuse series of Al I, and the sharp series of Tl I (375). Long absorption series of Al I, Ca I, In I and Tl I in the region $\geq 2000 \text{ \AA}$ have been observed. A great number of new absorption lines have been classified (375). Lines of multiply-ionized krypton, Kr XIII, have been obtained in the region 65–110 Å (262). The sequence of the atomic shell-filling and multiplicity of the main term has been studied theoretically (259). Hyperfine and isotopic structures for 275 lines of Pu have been analyzed. New data on the classification of the Pu spectrum have been obtained (264).

Of recent results of astrophysical interest obtained at Lund there should be mentioned the comprehensive description of the C I spectrum by L. Johansson (231a), the precision measurements by K. B. S. Eriksson of the red, green and ultraviolet forbidden lines of O I (136a) as well as the ultraviolet forbidden line of N I (136b), and work on S I by L. Jakobson (228a). A complete reinvestigation of Mg I by G. Risberg (400a) has enabled Swensson and Risberg (445a) to identify numerous new Mg I lines in the solar spectrum. The analysis of Fe IV by Edlén has yielded, so far, a practically complete set of levels of the ground configuration $3d^5$, which has provided identification of a number of forbidden transitions in RR Telescopii.

The urgent problem of providing the astrophysicist with data on analyses involves a revision of the published material in Volumes I, II, and III of *Atomic Energy Levels* and of the *Multiplet Tables*. This has been started in a new Series of pamphlets prepared for individual spectra for which analyses are essentially complete. Section 1 (322) deals with Si II, Si III and Si IV and is in print. Section 2 contains similar data on Si I; it is in press. Forthcoming Sections will include the spectra in Table 10.

Table 10. Spectra scheduled for Revised Compilation

H I sequence (4)					Na I			
Li I					Mg I	Mg II		
Be I	Be II				Al I		Al III	
C I	C II	C III	C IV		Si I			
N I	N II		N IV	N V	P I	P II		
O I					Ca I	Ca II		
	F II						Ti III	Ti IV

Revised analyses of most of these spectra have come from Lund. For Si I the analysis is chiefly from Purdue University, and for P I and P II it has been done at Princeton.

New Multiplet Tables are partially completed, also, for several more complex spectra listed in Table 11.

Table II. Spectra—Further Analysis Unlikely

Mn I	Mn II		Nb I	Nb II
		Fe III		Mo II
		Co III	Ru I	Ru II
		Ni III	I I	I II
Cu I	Cu II			Hf II

Kiess has directed work on a new description and analysis of Ti I (16) and is completing monographs on Mo I and Ta I, respectively. A new analysis of Hf I by Meggers was nearly finished at the time of his death.

At the National Bureau of Standards the reference catalogue on atomic spectra is being maintained as completely as possible.

ATLASES

Two important Atlases have been published at Castel Gandolfo by Fr. Junkes and his staff. Part One of *Atomic Spectra in the Vacuum Ultraviolet from 2250–1100 Å* (239) contains nine photographic charts (30 × 40 cm) of hollow cathode spectra of seven elements: Al, C, Cu, Fe, Ge, Hg, Si and the Lyman bands of molecular hydrogen from 1650–1260 Å as excited by a hydrogen lamp.

The second Atlas consists of sixteen photographic charts (24 × 30 cm) on which the Spectrum of Thorium from 9400–2000 Å is recorded, juxtaposed to the spectrum of the iron arc. The regions 9000–4000 Å and 2400–2000 Å are taken in the first order with a reciprocal dispersion 5 Å/mm; the region 4300–2400 Å is taken in the second order (238).

THE SOLAR SPECTRUM

The atlas of the Ultraviolet Solar Spectrum that is being prepared by Tousey and his staff at the Naval Research Laboratory is nearing completion. Some 7000 lines are listed between 3000 and 2090 Å. They have been observed on rocket spectrograms taken in flights in 1961 and 1964. About half of the lines have been identified, which indicates the urgent need for further laboratory work on atomic spectra.

A comparison of the solar spectrum in the range 170 to 220 Å with spectra of the Zeta plasma (Harwell) and with spectra of an Fe-loaded θ -pinch (NRL) shows that many of the strong solar lines must be due to Fe. Similar work on these identifications has been carried on independently by other groups, see for example p. 252, and papers by Gabriel and others at Culham (166). Spectroheliograms obtained in the light of these lines at NRL showed that they were emitted by the whole solar disk, indicating that intermediate ionization stages of Fe were mainly responsible. It was finally proposed by a number of workers that the solar lines could be produced by $3p$ - $3d$ transitions in Fe IX to Fe XIII,

Workers at Culham report that on 9 April, 1965 a spectrum of the chromosphere and corona in the range 950–2950 Å was obtained from the flight of a stabilized Skylark rocket (68). About 300 emission lines were observed, of which some 75% have been identified. New identifications include intersystem combinations in C III, N IV, O V and forbidden transitions in Fe XI and Fe XII (69).

It is a pleasure to report that the current revision of the 1928 edition of Rowland's Table of Solar Spectrum Wavelengths has at long last been completed. In 1948 the IAU requested Minnaert at Utrecht and Mrs Moore-Sitterly in Washington to carry out this project on a

cooperative basis. Since then the work has gone forward slowly but steadily. Minnaert and Houtgast have furnished the equivalent widths for more than 20 000 lines from the Utrecht Atlas, while Moore has revised and extended the identifications with the aid of the data collected for the 'Atomic Energy Levels' Program. Copies of the Monograph are available for distribution (323).

CHARLOTTE MOORE-SITTERLY
President of the Commission

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ADDENDA

On page 235, after the first alinea: 'In collaboration with . . .', add the following alinea:

Green, Johnson, and Kolchin (192a) have computed oscillator strengths in He I for all possible electric dipole transitions between the terms $n^{1,3} S$, $n^{1,3} P^0$, $n^{1,3} D$, where $n = 1$ to 9 for S terms, 2 to 8 for P^0 terms and 3 to 8 for D terms. Central-field wave functions with exchange and configuration interaction, were used. Oscillator strengths were computed by the length and velocity expressions.

On page 237, line 9, after: ". . . with the earlier theories for ion lines", add: "while typically consistent to $\pm 20\%$ with calculations for the case of arc lines."

Additional References

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