DIVISION B
COMMISSION 14

ATOMIC AND MOLECULAR DATA
DONNÉES ATOMIQUES
ET MOLÉCULAIRES

WORKING GROUP

MOLECULAR DATA
DONNÉES MOLÉCULAIRES

CHAIR

Steven R. Federman

VICE-CHAIRS

Peter F. Bernath, Holger S.P. Müller

TRIENNIAL REPORT 2012-2014

1. Introduction
The current report covers the period from the second half of 2011 to late 2014. It is divided into three areas covering rotational, vibrational, and electronic spectroscopy. A significant amount of experimental and theoretical work has been accomplished over the past three years, leading to the development and expansion of a number of databases whose links are provided below. Two notable publications have appeared recently: An issue of The Journal of Physical Chemistry A in 2013 honoring the many contributions of Takeshi Oka (J. Phys. Chem. A, 117, pp. 9305-10143); and IAU Symposium 297 on Diffuse Interstellar Bands (Cami & Cox 2014). A number of the relevant papers from these volumes are cited in what follows. Related research on collisions, reactions on grain surfaces, and astrochemistry are not included here.

2. Rotational Spectra
A large number of reports have appeared dealing with rotational spectra of molecules potentially relevant to radio-astronomical observations. Therefore, emphasis will be put on investigations dealing with molecules already observed in space, and on molecules related to these species. A few observational papers are mentioned to highlight some recent findings. The grouping of the molecules has been modified with respect to the previous report. Complex organic molecules are very important for ALMA, and they have attracted considerable attention in the last three years. They form the first group and include most of the so-called weed molecules. Molecules which (may) occur in circumstellar envelopes of late type stars form the second group. Additional groups deal with hydride molecules, with cations, or with other molecules. For completeness, we also include determinations of transition frequencies from radio astronomical observations, provided these are of sufficient importance.

Several databases provide rotational spectra of (mostly) molecular species of astrophysical and astrochemical relevance. The two most important sources for predictions generated from experimental data by employing appropriate Hamiltonian models are
the Cologne Database for Molecular Spectroscopy, CDMS† (Müller et al. 2001, 2005) with its catalog‡ and the JPL catalog¶ (Pickett et al. 1998). Both also provide primary information, i.e. laboratory data with uncertainties, mostly in special archive sections. Additional primary data are available in the Toyama Microwave Atlas∥. A useful resource on the detection of certain molecular transitions in space is the NIST Recommended Rest Frequencies for Observed Interstellar Molecular Microwave Transitions, which has been updated some years ago (Lovas 2004).

The European FP7 project Virtual Atomic and Molecular Data Centre, VAMDC††, aims at combining several spectroscopic, collisional, and kinetic databases. The CDMS is the rotational spectroscopy database taking part‡‡; recently, the JPL catalog has joined; several infrared databases are also involved. The project has been described by Dubernet et al. (2010).

Other tertiary sources combining data from various databases are, e.g., Cassis (http://cassis.cesr.fr/), which provides tools to analyze astronomical spectra, lamda (http://www.strw.leidenuniv.nl/~moldata/) which also contains collisional data, or splatalogue (http://www.splatalogue.net/). These databases rely heavily on the CDMS and JPL catalogs for their rotational data. This applies in part also to the infrared databases HITRAN and GEISA for selected rotational or rovibrational data.

2.1. Complex molecules

An overview of molecular complexity achievable with single dish radio telescopes is provided by Belloche et al. (2013). They carried out molecular line surveys of the giant molecular clouds Sagittarius B2(N) and (M) close to the Galactic Center with the IRAM 30 m telescope at 3 mm with additional observations at 2 and 1.3 mm. The detections include several new molecules, isotopologues, and excited vibrational states. Follow-up ALMA Cycle-0 observations resulted in the detection of the first branched alkyl compound, iso-C$_3$H$_7$CN (Belloche et al. 2014).

Zaleski et al. (2013) extended the rotational spectroscopy of cyanomethanimine and described the detection of the $E$ conformer, which is presumably higher in energy than the $Z$ conformer, but has a much larger dipole moment. Kolesniková et al. (2014) extended the ethyl mercaptan data sets considerably and concluded that the molecule would be present in Orion. We also emphasize investigations and astronomical detections of dimethyl ether with one D (Richard et al. 2013) or with one or two $^{13}$C (Koerber et al. 2013), as well as methyl formate in its doubly torsionally excited state (Kobayashi et al. 2013) or several of its isotopologues (Coudert et al. 2013; Haykal et al. 2014; Tercero et al. 2012). There was also an account on the rotational spectroscopy of the very high lying anti-conformer and its tentative detection in space (Neill et al. 2012).

Other reports include THz frequency (Pearson et al. 2011) and intensity studies (Fortman et al. 2014; McMillan et al. 2014) of CH$_3$OH, extensive studies of $^{13}$CH$_3$OH (Xu et al. 2014), CH$_2$DOH (Pearson et al. 2012; Coudert et al. 2014a), CH$_3$SH (Xu et al. 2012), and ethyl cyanide (Daly et al. 2013; Richard et al. 2012), as well as vinyl cyanide (Kisiel et al. 2012; Kraśnicki et al. 2011b; López et al. 2014), including redetermination of their dipole moment components (Kraśnicki & Kisiel 2011) with a considerable change in $\mu_b$ for vinyl cyanide.

† http://www.astro.uni-koeln.de/cdms/
‡ http://www.astro.uni-koeln.de/cdms/catalog
¶ http://spec.jpl.nasa.gov/
∥ http://www.sci.u-toyama.ac.jp/phys/4ken/atlas/
†† http://www.vamdc.org/
‡‡ http://cdms.ph1.uni-koeln.de/cdms/portal/
Ilyushin & Hougen (2013) presented a somewhat restricted reanalysis of the rotational spectrum of acetone in its ground and its two singly excited torsional states employing a new BELGI variant. This program may be very useful for a variety of two-top internal rotor problems.

Several promising molecules can be searched for in space because of greatly extended laboratory data, such as butanone (Kroll et al. 2013), n-butyl cyanide (Ordu et al. 2012), 1,2- (Bossa et al. 2014) and 1,3-propanediol (Smirnov et al. 2013), urea (Remijan et al. 2014), and 2-aminopropanitrile (Mollandal et al. 2012); data on 3-aminopropanitrile are still very limited.

In addition, there are now several minor isotopologues for which searches are now viable: e.g. several isotopologues of methanimine (Motoki et al. 2014) and cyanamide (Kraśnicki et al. 2011a), deuterated formamide (Kutsenko et al. 2013), 13C-containing ethanol (Bouchez et al. 2012b), and deuterated (Bouchez et al. 2012a) and 13C-containing glycolaldehyde (Haykal et al. 2013).

Other studies involve H2CNH (Dore et al. 2012), H2CCNH (Degli Esposti et al. 2014), n-butanal (Hotopp et al. 2012), acetic acid (Ilyushin et al. 2013), aminoacetonitrile (Motoki et al. 2013) and methyleneaminoacetonitrile (Motiyenko et al. 2013), methylamine (Motiyenko et al. 2014), methyl acetate (Nguyen et al. 2014), acetaldehyde (Smirnov et al. 2014), and deuterated methyl cyanide (Nguyen et al. 2013).

2.2. Circumstellar molecules

In recent years, several molecular species were detected first in O-rich circumstellar envelopes (CSEs) of late-type stars. One recent prominent example is TiO2, a dust-forming molecule, detected in the CSE of VY CMa (Kamiński et al. 2013). Initially, detections of molecules in CSEs were commonly made toward C-rich stars, in particular CW Leonis, also known as IRC +10216. Remarkable examples are the laboratory spectroscopy and detection of HMgNC (Cabezas et al. 2013) and the rotational spectroscopy of FeCN and FeNC (Flory & Ziurys 2011); the detection of FeCN was reported earlier, though.

Investigations of detected species involve 29 SiC2 and 30 SiC2 (Kokkin et al. 2011) and SiO (Müller et al. 2013) along with an analysis of recent NaCN data (Müller et al. 2012b). SiC2 spectroscopic parameters were improved once more through radio astronomical observations (Müller et al. 2012a).

Further investigations include ScS and YS (Adande et al. 2012), 25 MgH and 67 ZnH (Buchino & Ziurys 2013), KSH (Buchino et al. 2013), AlC3N (Cabezas et al. 2014), PCN (Halfen et al. 2012), PH2CN (Halfen et al. 2014), SiC3H (Kokkin et al. 2014), SiC2N and SiC3N (Umeki et al. 2014), alkali metal acetylides (Sheridan et al. 2011), and AlCCH (Sun et al. 2012). Halfen & Ziurys (2014) reported a transition frequency for the AlH J = 2 − 1 transition which is not compatible with numerous IR and optical studies. Therefore, we recommend to avoid using this datum until further clarification.

2.3. Hydrides

Hydrides are here all molecules consisting of one non-metal atom and one or more H atoms. They may be neutral or charged. Metal hydrides have been dealt with in subsection 2.2. Even though the Herschel mission was terminated late in April 2013, data are still being analyzed; for instance, quite recently the detection of ArH+ was reported (Barlow et al. 2013; Schilke et al. 2014). Moreover, the German REceiver At Terahertz frequencies (GREAT) on board of the Stratospheric Observatory For Infrared Astronomy (SOFIA) has opened new observing capabilities above 1 THz. In addition, transitions of heavier hydrides or higher rotationally excited transitions of lighter asymmetric
top hydrides, such as H₂O, can be observed from the ground and may be of particular importance for ALMA.

Noteworthy is especially the investigation of HCl⁺ (Gupta et al. 2012), which was important to establish its detection in the ISM. We point out also extensive studies of H₂O (Yu et al. 2012b, 2013; Coudert et al. 2014). Drouin et al. (2011) reported not only transition frequencies of H₂O around 2.6 THz, but also of HD and NH₃. Noteworthy are also the extensive investigations on sulfur isotopologues of H₂S (Azzam et al. 2013; Cazzoli & Puzzarini 2014; Cazzoli et al. 2014) and those of H₂F⁺ (Amano et al. 2012). Although H₂F⁺ is predicted to have small column densities in space, it is necessary to know selected transitions, in particular those involving the ground states, well enough.

Other studies include investigations of H₅O⁺ (Yu & Pearson 2014), NH₂ (Martin-Drumel et al. 2014), ¹⁵NH (Bailleux et al. 2012), several OH isotopologues (Drouin 2013), OH⁻ (Jusko et al. 2014), CH (Martin-Drumel et al. 2011; Truppe et al. 2014), and an analysis of PH₃ rotational data (Müller 2013). Müller et al. (2014) determined improved spectroscopic parameters for SH⁺ based on radio astronomical observations of the lowest frequency transitions.

2.4. Cations

Cationic light hydrides were mentioned in subsection 2.3. With regard to heavier cations, the laboratory spectroscopy of C₃H⁺ (Brünken et al. 2014) is particularly worth mentioning as it confirmed the earlier assignment of a long series of U-lines detected in the Horsehead Nebula mentioned in our last report. Gupta et al. (2013) reported on the rotational spectrum of H₂NCO⁺ and its tentative detection in Sgr B2(N).

Other studies involve CO⁺ (Spezzano et al. 2013), HNNO⁺ (McCarthy et al. 2013), HOSO⁺ (Lattanzi et al. 2011), C₂H₃CNH⁺ (Martinez et al. 2013), and Terahertz spectra of N₂H⁺, HCO⁺, and CF⁺ (Cazzoli et al. 2012).

2.5. Other molecules

We emphasize a study of several isotopologues of c-C₃H₂ (Spezzano et al. 2012), which led to the detection of c-C₃D₂. Other investigations, which may be worthwhile mentioning, include HCOOD and DCOOH (Cazzoli et al. 2011), the vinoxy radical (Endo & Nakajima 2014), HOOD (however with no transition frequencies) (Herberth et al. 2012), phenol (Kolesniková et al. 2013), HOSO (McCarthy et al. 2013), and an analysis of several O₂ isotopologues in several electronic states (Yu et al. 2012a).

3. Vibrational Spectra

The vibration-rotation spectra of molecules of astronomical or of potential astronomical interest are reviewed for the period 2011-2014 starting from the end of our previous report (Federman et al. 2012). In addition to the references to particular molecules given below, there are a number of spectral database compilations that are useful. Perhaps the most helpful is the HITRAN database that contains vibration-rotation line parameters for a large number of species such as H₂O, CO₂, CO, HF and so forth, found primarily in the Earth’s atmosphere. A new edition has appeared (HITRAN 2012, Rothman et al. 2013); further information including updates and corrections is available†. The molecular coverage is slowly being expanded to cover planetary atmospheres other than Earth and HITRAN 2012 contains line parameters for PH₃, H₂, and CS. HITRAN is widely used for astronomical applications although it is not always suitable because of missing lines

† http://www.cfa.harvard.edu/hitran/
and bands, particularly in the near infrared region. For high temperature applications, the HITTEMP database (Rothman et al. 2010) for H₂O, CO₂, CO, NO, and OH is more suitable and a new edition is being prepared.

For larger molecules, individual vibration-rotation lines are no longer clearly resolved and it becomes necessary to replace line-by-line calculations by absorption cross sections. The main drawback to using cross sections is that a considerable number of laboratory measurements are needed to match the temperature and pressure conditions of the objects under observation. HITRAN also includes a number of high resolution infrared absorption cross sections for organic molecules such as methanol, ethane, and acetone, but the broadening gas is air rather than H₂, N₂, or CO₂. While the GEISA database has significant overlap with HITRAN, it contains additional molecules of interest for studies of planetary atmospheres (Jacquinet-Husson et al. 2011).

There are a number of web sites that have collections of spectroscopic line lists or infrared absorption cross sections that are updated regularly. The ExoMol site† of J. Tennyson has an extensive collection of calculated line lists designed “as input to atmospheric models of exoplanets, brown dwarfs and cool stars.” G. Villanueva’s site‡ provides line lists for the simulation of infrared emission spectra of comets for species such as ethane, methanol, ammonia, and water excited by solar radiation. A very useful set of infrared absorption cross sections for several hundred molecules are available from Pacific Northwest National Laboratory¶, PNNL, for the 600-6500 cm⁻¹ (1.54-16.7 μm) range (Sharpe et al. 2004). While the PNNL spectra are not always suitable for astronomical applications because they are recorded with 1 atm of nitrogen as a broadening gas at sample temperatures of 278, 293, and 323 K, they can be very useful.

Other interesting sources of infrared data are the ACE high resolution spectral atlases of the Sun (Hase et al. 2010) and of the Earth’s atmosphere (Hughes et al. 2014) recorded using a high resolution Fourier transform spectrometer in low Earth orbit. The ACE atmospheric spectra are recorded by solar occultation (i.e., using the Sun as a light source during sunrise and sunset). This geometry matches that used for exoplanet transit spectroscopy (Bernath 2014) so these spectra are a template for infrared absorption spectra of Earth-like planets.

3.1. Diatomic molecules

Hydrogen is the most abundant element in the Universe so it is no surprise that small diatomic hydrides are also abundant. One of the major successes of the Herschel Space Observatory was the detection of many diatomic hydrides, often for the first time, by rotational spectroscopy (Benz et al. 2013). Diatomic hydrides have large rotational constants so their pure rotational spectra fall in the Terahertz region where absorption by the Earth’s atmosphere is a problem. With Hershel no longer operational, infrared observations from the ground with instruments such as Phoenix, CRIRES, and TEXES are attractive. The new EXES instrument on the SOFIA (Stratospheric Observatory for Infrared Astronomy) aircraft is particularly promising because it flies in the stratosphere above most of the Earth’s atmosphere.

The argonium ion (³⁶ArH⁺) was detected in the Crab Nebula by Barlow et al. (2013) using Herschel. On Earth the major isotope is ⁴⁰Ar from radioactive decay of ⁴⁰K in rocks while ³⁶Ar is the main isotope in stars because of nucleosynthetic production in supernova explosions. Improved vibration-rotation spectra of the 1-0 band of ³⁶ArH⁺

† http://www.exomol.com/
‡ http://astrobiology.gsfc.nasa.gov/Villanueva/spec.html
¶ http://nwir.pnl.gov
and $^{38}\text{ArH}^+$ were reported by Cueto et al. (2014). Improved line positions have also been measured for $\text{HeH}^+$ by Perry et al. (2014).

The vibration-rotation line parameters of the hydrogen halide molecules (HF, HCl, HBr, and HI) have been revised in HITRAN 2012. Of particular interest in astronomy are the extensive lists of new line positions and intensities for HF and HCl that are used to obtain fluorine (Jönnson et al. 2014) and chlorine abundances. A similar extensive revision of the CH, NH, and OH line parameters has been carried out. These new line lists were created using reliable dipole moment functions and inclusion of the Herman-Wallis effect using LeRoy’s LEVEL computer program†. The CH line list of Masseron et al. (2014) primarily focuses on electronic transitions but also includes vibration-rotation bands. The NH (Brooke et al. 2014a) and OH (Brooke et al. 2015) work adds line intensities to our previous analyses of line positions based partly on the ACE solar spectrum.

The ExoMol line lists include BeH, MgH, CaH (Yadin et al. 2012), SiO (Barton et al. 2013), NaCl, KCl (Barton et al. 2014), and PN (Yorke et al. 2014). These new line lists combine experimental measurements and ab initio calculations. Salt vapors such as NaCl and KCl are predicted to be present in hot super-Earth exoplanets (Schaefer et al. 2012). The infrared bands of SiO are readily observed in K-M giant and supergiant stars (Ohnaka 2014).

The vibration-rotation bands of H$_2$ are forbidden by electric dipole selection rules, but are observable by weak electric quadrupole transitions. The line intensities and line positions of the vibration-rotation bands of H$_2$ were recalculated for HITRAN 2012 based on ab initio results (Rothman et al. 2013). The line positions are estimated to have an accuracy of about 0.001 cm$^{-1}$ and more recent results from calculations (Pachucki & Komasa 2014) and experiments (Cheng et al. 2012) have even higher accuracy. The HD molecule is polar and so has dipole-allowed transitions, which are also reported in HITRAN 2012.

The CN radical is found in a very wide range of sources mainly by radio and optical/IR astronomy. However, vibration-rotation lines can also be detected (Wiedemann et al. 1991) and new line lists for CN that include the vibration-rotation bands for CN (Brooke et al. 2014b), $^{13}$CN, and C$^{15}$N (Sneden et al. 2014) have been generated with an ab initio dipole moment function calculated by D. Schwenke (NASA-Ames). These extensive line lists are based on recent laboratory observations of the $B^2\Sigma^+ - X^2\Sigma^+$ and $A^2\Pi - X^2\Sigma^+$ Violet System and Red System, which extends into the near IR spectral region. A new line list has been completed for the corresponding infrared $A^2\Pi - X^2\Sigma^+$ electronic transition of the isovalent CP radical (Ram et al. 2014a). The Ballik-Ramsay and Phillips Systems of C$_2$ are also prominent in the near infrared and a new perturbation analysis has demonstrated that the singlet-triplet splitting was in error by 3 cm$^{-1}$ (Chen et al. 2015). This analysis has astronomical implications for example in the excitation of C$_2$ in comets by solar radiation.

An important application of molecular line parameters is to extract elemental abundances from the near infrared spectra of large numbers of cool stars observed in surveys such as APOGEE (Apache Point Observatory Galactic Evolution Experiment). APOGEE is recording H-band (1.51-1.69 μm) spectra of thousands of evolved, late-type stars with a focus on red giants with a surface temperature of 3400-5000 K (Cottaar et al. 2014). CNO abundances are derived from CO and OH overtone spectra, and the Red System of CN. The improved line parameters for OH and CN, along with HITTEMP values for CO cited above, are recommended for abundance analyses. Stellar models also

† http://leroy.uwaterloo.ca/programs/
require dissociation energies and significant improvements have been made using the method of Active Thermochemical Tables‡. For example, the latest values for the dissociation energies $D_0$ for C$_2$, CH, CO, CN, and OH are (in eV) 6.24475, 3.57154, 11.11092, 7.72400, and 4.41129, respectively (Ruscic et al. 2014).

3.2. Small polyatomic molecules

The line parameters of ammonia (Down et al. 2013) and methane as given in the HITRAN 2012 database are satisfactory for most astronomical purposes at low temperatures, except for overtone and combination bands in the near infrared and visible regions. In the near infrared, Sung et al. (2012) have generated an empirical line list for NH$_3$ covering the 6300 to 7000 cm$^{-1}$ region. By using spectra recorded over a range of sample temperatures (185-296 K), empirical lower state energies were obtained, although most of the lines still lack detailed quantum number assignments. Similar work in Grenoble (Campargue et al. 2013) on CH$_4$ has provided the WKLMC empirical line lists (5852-7919 cm$^{-1}$) using two temperatures (80 K and 296 K). The WKLMC methane line list is a major improvement on the band models typically used by planetary astronomers. New measurements for methane spectra in the 4800-5300 cm$^{-1}$ region have been reported by Nikitin et al. (2014). For PH$_3$ (long detected in Jupiter and Saturn) a new analysis for the 5 bands that comprise the pentad region between 1950 and 2450 cm$^{-1}$ has appeared (Devi et al. 2014). Work on high overtone and combination bands of CO$_2$ continues (Petrova et al. 2013; Lu et al. 2013) for applications for Venus and Mars.

The spectra of hot molecules needed to simulate the spectra of cool stars, brown dwarfs, and exoplanets remains a challenge. For hot water, calculations continue to improve (Polyansky et al. 2013), but the BT2 line list (Barber et al. 2006) remains the standard for astronomical applications. A new extensive compilation of the vibration-rotation energy levels of water has appeared (Tennyson et al. 2013). For hot ammonia, laboratory spectra recorded in emission are available (Hargreaves et al. 2011, 2012a) and with at least two groups providing rather good calculated spectra (Huang et al. 2011a,b; Yurchenko et al. 2011). There is much recent progress on the spectroscopy of hot methane with the experimental line lists of Hargreaves et al. (2012b) and two comprehensive calculated line lists (Yurchenko & Tennyson 2014; Rey et al. 2014a); a calculation for CH$_3$D has also been carried out (Rey et al. 2014b). For CO$_2$, HITRAN 2012 for cold molecules and HITEMP, CDSD-4000 (Tashkun & Perevalov 2011) and calculations for 13 isotopologues for hot molecules (Huang et al. 2014) are recommended. New internal partition functions for NH$_3$ and PH$_3$ (Sousa-Silva et al. 2014) have been published. A new line list for HCN and HNC has been prepared by Barber et al. (2014) combining both experimental and theoretical work.

The pure rotational spectrum of NH$_3$D$^+$ has been tentatively identified in Orion (Cernicharo et al. 2013), based on a new infrared laboratory spectrum (Doménech et al. 2013). H$_2$Cl$^+$ has been detected by Herschel, but not H$_2$F$^+$; new infrared spectra of H$_2$F$^+$ have been measured with a Fourier transform spectrometer (Fujimori et al. 2013).

The carbon chain molecules C$_3$ and C$_5$ can be detected in the circumstellar envelopes of carbon stars by infrared observations (Hargreaves et al. 2014). Improved laboratory spectra of C$_3$ have been reported in the 3 μm region (Krieg et al. 2013) and high resolution photoelectron spectroscopy has been used to refine the vibrational frequencies of C$_5$ (Weichman et al. 2013).

‡ http://atct.anl.gov/
3.3. Large molecules

There is continuing strong interest in large carbon-containing molecules such as C\textsubscript{60} (e.g., Berné & Tielens 2012) and polycyclic aromatic hydrocarbons (PAHs). For PAH molecules the NASA-Ames database has been updated and new features added (Boersma et al. 2014). Extensive calculations by the NASA-Ames group have continued, for example, on dehydrogenated PAHs (Mackie et al. 2014) and PAH clusters (Ricca et al. 2013). High resolution infrared absorption spectra of the $\nu_{68}$ mode of pyrene near 1184 cm$^{-1}$ were recorded by Brumfield et al. (2012). ZEKE photoelectron spectroscopy was used to measure the frequencies of the benzoperylene cation (Zhang et al. 2012). There is continuing discussion on the nature of these ‘PAH’ bands in astronomical sources, for example with the suggestion that mixed aromatic/aliphatic organic nanoparticles, MAONs, rather than free flying PAHs are the carrier (Kwok & Zhang 2013). Improved infrared absorption spectra of C\textsuperscript{+}\textsubscript{60} and C\textsubscript{−}\textsubscript{60} in neon matrices have been measured by Kern et al. (2013) and C\textsuperscript{+}\textsubscript{60} has been identified in emission in the interstellar medium (Berné et al. 2013).

4. Electronic Spectra

Recent work on electronic spectra, such as line identification, energy levels, and related data needed for photochemical models, are described. These data include absorption cross sections (or equivalently lifetimes, transition probabilities, and oscillator strengths), predissociation widths and rates, and analyses of anomalies in line strength and width caused by perturbations between energy levels. Both empirical (experimental and astronomical) and theoretical results are presented. The section is divided into four topics: interstellar matter, including diffuse molecular clouds, disks around newly formed stars, and comets whose chemistry is similar; metal hydrides and oxides in the atmospheres of late-type stars; the atmospheres of planets and their satellites; and larger molecules. Although some of the work is noted in the sections on rotational and vibrational spectra, electronic spectroscopy is stressed here.

4.1. Interstellar matter

Because observations and analyses of CO and its photochemistry is central to astrophysical studies, a large body of new work has appeared since the last report. Oscillator strengths and predissociation rates with improved precision are now available for a number of transitions in CO isotopologues (Eidelsberg et al. 2012, 2014; Heays et al. 2014a; Stark et al. 2014); another study focused on self shielding among the isotopologues (Chakraborthy et al. 2012). Since CO photodissociation involves line absorption, self shielding, which arises when dissociating transitions become optically thick, allows molecules in the cloud interior to be protected. A theoretical study on predissociation in the E state (Majumder et al. 2014) obtained a line width consistent with earlier measurements. Using a newly developed technique, Ng and colleagues (Gao et al. 2011a, 2012, 2013a,b) measured branching fractions for the atomic products arising from dissociation for specific rotational levels. Branching fractions were also obtained for other systems, including CO\textsubscript{2} and N\textsubscript{2} (Gao et al. 2011b; Pan et al. 2011; Lu et al. 2014) as well as O\textsubscript{2} (Holland & Shaw 2012; Zhou et al. 2014a). Similar studies involve N\textsubscript{2} photoionization (Holland & Shaw 2012; O’Keeffe et al. 2012) and CO\textsubscript{2} photoionization (Furch et al. 2013).

New measurements of the Ångström ($B^{1}\Sigma^{+} - A^{1}\Pi$) and fourth positive ($A^{1}\Pi - X^{1}\Sigma^{+}$) systems improved our knowledge of the perturbations affecting the A state. Hakalla & Zachwieja (2012) and Hakalla et al. (2013) studied Ångström system bands in the rare
$^{13}\text{C}^{17}\text{O}$ isotopologue; Hakalla and colleagues obtained spectra for these bands in other isotopologues (Hakalla et al. 2012a,b; Kepa et al. 2014; Hakalla et al. 2014). As for the $A$–$X$ system of bands, Kepa et al. (2011) and Gavilan et al. (2013) provided further details on the perturbations in $^{13}\text{C}^{16}\text{O}$, while Niu et al. (2013) analyzed $^{12}\text{C}^{16}\text{O}$ spectra. Lifetimes for the main isotopologue were obtained by Blokland et al. (2011). A time-dependent quantum mechanical study (Majumder et al. 2012) yielded oscillator strengths; the slight differences with experimental results likely arise from perturbations in the $A$ state. Moreover, accurate line positions were measured for transitions that are sensitive to the proton-to-electron mass ratio (de Nijs et al. 2011; Salumbides et al. 2012; Niu et al. 2015), and de Nijs et al. (2013) tested mass-scaling relations among isotopologues for the $a^3\Pi$ state.

Since $\text{N}_2$ and $\text{CO}$ are isoelectronic, photochemical models of interstellar environments need to take this into account (Heays et al. 2014b). Much like the studies on CO discussed above, new experimental results on oscillator strengths and predissociation (Heays et al. 2011; Wu et al. 2012) were reported. Cross sections for electron-impact excitation (Malone et al. 2012) and photoionization efficiencies for $\text{N}_2$ isotopologues (Randazzo et al. 2014) were obtained as well. Little & Tennyson (2013) studied the singlet and triplet states of $\text{N}_2$ through ab initio calculations. Wu et al. (2013) characterized far ultraviolet absorption of $\text{N}_3$ and $\text{N}_3^+$ in an $\text{N}_2$ matrix.

Other simple carbon-bearing molecules received attention in the past three years. Measurements on the Swan band system ($d^3\Pi$–$a^3\Pi$) in $\text{C}_2$ produced new molecular constants for several bands (Chan et al. 2013; Yeung et al. 2013; Bornhauser et al. 2013) and line strengths for others including the $^{12}\text{C}^{13}\text{C}$ isotopologue (Brooke et al. 2013; Ram et al. 2014b). Higher-lying vibrational levels in the $X$, $A$, $a$, and $d$ states were observed by Nakajima & Endo (2013); they also analyzed perturbations seen in the $v = 8$ level of the $d$ state. Nakajima & Endo (2014) described further studies of the $d^3\Pi_g$–$e^3\Sigma^+_u$ band system. Hupe et al. (2012) analyzed perturbations involving the $F$ state that were seen in astronomical spectra. An ab initio study by Schmidt & Bacskey (2011) provided spectroscopic constants for a newly identified quintet state. The $A^2\Pi$–$X^2\Sigma^+$ and $B^2\Pi$–$X^2\Sigma^+$ band systems in CN and its isotopologues were studied by Bernath and colleagues. Spectroscopic results on $^{12}\text{C}^{15}\text{N}$ (Colin & Bernath 2012), $^{13}\text{C}^{14}\text{N}$ (Ram & Bernath 2012), and $^{13}\text{C}^{15}\text{N}$ (Colin & Bernath 2014) were published, and line strengths in the form of oscillator strengths were derived for $^{12}\text{C}^{14}\text{N}$ (Brooke et al. 2014b) and its isotopologues (Saened et al. 2014). Hyperfine structure in spectra of the $A$–$X$ band was discussed by Forthomme et al. (2014). Recent theoretical efforts on CN involved molecular properties of its low-lying electronic states (Shi et al. 2011a) and the determination of photodissociation cross sections (El-Qadi & Stancil 2013). Two studies on $\text{C}_3$ appeared; one provides laboratory spectra on $A$–$X$ bands for $\text{C}_3$ and its isotopologues (Haddad et al. 2014) and the other gives oscillator strengths for a number of these bands based on astronomical measurements (Schmidt et al. 2014).

Studies also focused on other species found in interstellar clouds and comets. Theoretical work appeared on photoabsorption and photodissociation for $\text{H}_2$ (Mezei et al. 2014), $\text{HeH}^+$ (Loreau et al. 2013; Miyake et al. 2011), $\text{ArH}^+$ (Roueff et al. 2014), $\text{LiH}^+$ (Bovino et al. 2011), $\text{NH}_3$ (Chatterley et al. 2013), and $\text{H}_2\text{O}$ (Jiang et al. 2011b; Zhou et al. 2014b). Low-lying states in CS were studied theoretically by Shi et al. (2011b), and Ponzi et al. (2014) reported theoretical calculations on CS photoionization. Calculations on low-lying states of $\text{HCl}$ (Engin et al. 2012) were performed as well. Experimental lifetimes on the $A^2\Pi$ state of $\text{NH}_2$ were measured by N’Doumi & Halpern (2012). Photoionization cross sections for $\text{CO}$, $\text{N}_2$, and $\text{H}_2\text{O}$ were also determined theoretically.
(Ruberti et al. 2014). It is also worth noting a compilation of transition probabilities for several diatomic species (Billoux et al. 2014).

4.2. Late-type stars
During this reporting period, new results on MgH, FeH, and ZrO were published. Hinkle et al. (2013) identified lines from isotopologues of MgH associated with the A–X system, and GharibNezhad et al. (2013) provided transition probabilities for lines of the A–X and B′–X systems for the main isotopologue. Furthermore, Zhang & Steimle (2014) conducted Zeeman spectroscopy on the A–X (0,0) band. An ab initio study of the A and B′ states of MgH also yielded transition probabilities (Mostafanejad & Shayesteh 2012). Low-lying electronic states of FeH were described by theory (DeYonker & Allen 2012), as were the 1^1Π–X^1Σ+ and 1Σ+–X^1Σ+ systems of ZrO (Shanmugavel & Sriramachandran 2011), where the latter study presented data including oscillator strengths.

4.3. Planetary atmospheres
The molecules CO$_2$ and SO$_2$ continue to draw attention by experimentalists and theorists. Photoabsorption cross sections for electronic transitions in CO$_2$ were obtained through experimental measurements (Archer et al. 2013; Venot et al. 2013) and theoretical calculations (Grebenshschikov 2012, 2013). Low-lying electronic states were also studied theoretically (Zhou et al. 2013). As for SO$_2$, excited state dynamics were studied experimentally (Wilkinson et al. 2014) and theoretically (Mai et al. 2014; Lévêque et al. 2014), while Xie et al. (2013) determined potential energy surfaces for the two lowest singlet and two lowest triplet states.

Data needs for other molecules were also addressed. Absorption cross sections for isotopologues of SO were obtained theoretically by Danielache et al. (2014). A global fit to transitions across the spectrum for O$_2$ yielded isotopically invariant data for the X, a, and b states (Yu et al. 2012a), from which an detailed analysis of the airglow bands was accomplished (Drouin et al. 2013). Measurements on absorption cross sections for C$_2$H$_2$ (Cheng et al. 2011) were also reported.

4.4. Larger Molecules
Most studies of electronic transitions in large molecules seek correspondences with wavelengths associated with diffuse interstellar bands. Here we give a sampling of the efforts in this area. PAH-related species have drawn considerable attention. Recent spectroscopic measurements included results on neutral species by Gredel et al. (2011) and on ionized species by Garkusha et al. (2011), Bonaca & Bilalbegović (2011), and Hardy et al. (2013). A combined experimental and theoretical study on propadienylidene (C$_3$H$_2$) was conducted by Stanton et al. (2012). Chakrabarty et al. (2013) measured the spectrum of the triacetylene cation. A theoretical computation by Majumdar et al. (2014) provided the spectrum of the cyanomethyl anion (CH$_2$CN$^-$). The photoionization of cyanoacetylene was also the focus of an experimental study (Leach et al. 2014).

Steven R. Federman
chair of Working Group

References
Berné, O. & Tieblen, A. G. G. M. 2012, PNAS, 109, 401
Billoux, T., Cressault, Y., & Gleizes, A. 2014, JQSRT, 133, 434
Bouchez, A., Walters, A., M¨uller, H. S. P., et al. 2012b, JQSRT, 113, 1148
Drouin, B. J. 2013, J. Phys. Chem. A, 117, 10076
Hakalla, R., Zachwieja, M., & Szajna, W. 2014, JQSRT, 140, 7
Hargreaves, R. J., Li, G., & Bernath, P. F. 2012a, JQSRT, 113, 670