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MOLECULAR OPACITY DATA FOR STELLAR ATMOSPHERES

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RESUMEN. Presentamos una revisión de los datos sobre opacidades moleculares que se disponen de diferentes fuentes, y comparamos los métodos que se usaron para calcularlos. En las bases de datos astrofísicos, actualmente existen intensidades de línea, energías de excitación y frecuencias para 22 millones de líneas provenientes de 20 moléculas diatómicas diferentes y 35 millones de líneas de 4 moléculas poliatómicas, lo cual es insuficiente para interpretar las observaciones de satélites que se acumulan especialmente en el infrarrojo. También faltan datos para modelos computacionales efectivos de atmósferas, y además nunca se ha analizado la calidad y el efecto de gran parte de estos datos sobre las líneas débiles. No se conoce prácticamente nada sobre la opacidad de las móleculas mayores que se observan, o que se sospecha que existen, en los envolventes circun-estelares, y su posible presencia en la fotosfera superior puede cambiar considerablemente nuestro concepto de las atmósferas de las estrellas frías. Se revisa el progreso reciente en el entendimiento de este nuevo campo y su probable importancia en las atmósferas estelares.

ABSTRACT. We review here the molecular opacity data that are available from various sources, and compare the methods that have been used in computing them. Line strengths, excitation energies and frequencies for 22 million lines of 20 different diatomic molecules and 35 million lines of 4 polyatomic molecules exist in astrophysical data bases, which is probably far from sufficient for interpretation of the accumulating amount of satellite data especially in the infrared. Also, data are lacking for good model atmospheric computation, and the quality and effect of a great fraction of the data on the weak lines have never been analysed. Practically nothing is known about the opacity of the bigger molecules that are observed or suspected in the circumstellar envelopes (CSE), and their possible presence in the upper photosphere may substantially alter our picture of cool stellar atmospheres. We review the recent progress in the understanding of this new field and its possible importance for stellar atmospheres.

Key words: MOLECULAR PROCESSES – OPACITIES – TRANSITION PROBABILITIES

I. INTRODUCTION

During recent years it has become well known that many weak lines of molecular bands play a crucial role in the atmospheric structure of stars and/or in the overall form of stellar spectra. Yet only few really weak bands have been observed in the laboratory, and discrepancies of a factor 2 to 4 between independent measurements of intensities are not uncommon. The uncertainty in the theoretical predictions of the strength of most weak bands is relatively big, because of an increasing difficulty in computing the correct energy and dipole moment when the molecule is far from equilibrium, and the *ab initio* methods hardly allow for an internal uncertainty estimate themselves. Since high-quality observed data on bands involving high-energy levels (i.e. the weak bands) are sparse, it is therefore very hard to judge the accuracy of the computed bands, and for the few molecules that

have been considered by more than one group, there is no existing comparison of their results. There is a lack both of molecules considered in the data bases and of completeness in the computations, and foremost there is a lack of knowledge about which amount of completeness and accuracy is needed for various purposes. It has very lately been realized that this is a serious problem in our ability to interpret the wealth of spectroscopic data incoming from the increasing number of satellites with access to the electromagnetic spectrum outside the visual range. During the IAU General Assembly 1991, three days of sessions were devoted to the discussion of atomic and molecular data. Only very little concrete news was presented concerning molecular data, and several speakers characterized the situation as a data crisis in astronomy.

I will review here the existing molecular opacity data and try to comment on the methods used by the various authors. It is not my intention to try to summarize directly the wealth of papers reporting laboratory data on individual lines and bands of various molecules; but the laboratory work will be described indirectly through the description of the opacity data, since these are necessarily based on compilation of observed data, use of molecular constants from observed data, or in other way, use of as many observed data as possible. The most comprehensive data bases of observed molecular line frequencies and intensities are the American Hitran data base (Rothman 1986, Rothman et al. 1987; 348 000 lines from 28 different molecules + two more molecules, COF_2 and SF_6, added to the list after 1987) and the French GISA data base (Husson et al. 1986). They are both available on magnetic tapes on request to the authors mentioned above. A recent conference on Molecular Spectroscopic Data Bases (13–14 June 1991, ed. L.S. Rothman) is to be published as a special issue of JQSRT. Very recommendable general information and references to laboratory data can frequently be found in the JANAF tables and in the Berkeley Newsletter. S.P. Davis and J.G. Phillips, who are editors of the Berkeley Newsletter, have throughout the years measured a number of band systems of particular astrophysical interest, which are kindly put at the disposal of the community by request to Davis or Phillips (see Davis 1987 for a review). These data are laboratory measured lines and therefore represent data on the basis of which constants can be calculated for computations of astrophysical opacities, or they can be used directly for synthetic spectrum calculations. The data include lines from the band systems of TiO (Davis et al. 1986), ZrO and YO (Littleton and Davis 1985), CN, FeH and LaO.

II. DIATOMIC MOLECULES

In four papers Chackerian, Piñeiro and Tipping have discussed the absorption coefficients of the isovalent diatomic molecules SiO (Tipping and Chackerian 1981), CO (Chackerian and Tipping 1983), CS (Piñeiro et al. 1987a), and SiS (Piñeiro et al. 1987b). The investigation is an attempt to combine theoretical and experimental data to obtain the best possible values for a complete set of transitions. For SiO, electronic bands with $\Delta v=0-6$, $v=0-15$, and $J\leq 115$ and the isotopes (28,16), (29,16), (30,16), (28,18) (numbers referring to the atomic mass of Si and O, respectively) were considered. For CO the corresponding numbers were $\Delta v=0-4$, $v=0-27$, $J\leq 150$, and (12,16), (12,17), (12,18), (13,16), (13,18), whereas they were $\Delta v=0-4$, $v=0-20$, $J\leq 200$, and (12,32), (12,33), (12,34), (13,32) for CS, and $\Delta v=0-4$, $v=0-5$, $J\leq 10$, and (28,32) for SiS. The authors offer their results on magnetic tapes on request. Their method in all the studies is to fit Dunham-type coefficients to experimental data in order to determine the potential energy function, and to express the dipole moment (as function of the stretching coordinate) analytically by use of a combination of experimental and theoretical data. From the potential energy function the eigenenergies and wavefunctions are found by numerical solution of the Schrödinger equation. Once the dipole moment function, M(x), is known the transition moment, $R = \langle vJ|M(x)|v'J'\rangle$, can be computed for all allowed transitions. This will give a complete description of the spectrum for the whole range of stretching displacements where M(x) is valid, and it is therefore not dependent on laboratory measurements of all the bands. In the standard treatment, the dipole moment function is described as a power series, $M(x) = M_0 + M_1x + M_2x^2 + ...$, which is usually a good description if the stretching displacement is not too far from equilibrium. In the case of SiO, where extensive *ab initio* calculations of the dipole moment exist, Tipping and Chackerian have shown that the *ab initio* dipole moment curve far from equilibrium can be described better by a Padé approximant, $M(x) = P_1(x)/P_2(x)$, where $P_2(x)$

is a polynomial of order four higher than the order of $P_1(x)$. The difference in the order of the two polynomials ensures the theoretical correct dependence for large stretching displacement. The authors conclude that their line strengths are accurate to 10% even for the weakest transitions, which, if correct, is considerably better than many other data in use, and they give very "user-friendly" expressions for computation of opacities from their results. The main drawback is that their fitting formulas cannot be extended to the dissociation limit, which is desirable for stellar purposes. For example, the highest vibrational level considered in the computations for CS is v = 20, which corresponds to approximately E = 26 000 cm^{-1}or less than half the value of the dissociation energy. In their final paper (on SiS) the authors compare the results of the four isovalent molecules, and they demonstrate that the transition moments for CO, CS, and SiO are very similar to one another. This fact is used to help construct the dipole moment curve for SiS, which is much less studied than the three other molecules in the laboratory as well as theoretically. Due to the sparse data for SiS, the dipole moment function for this molecule was not fitted with a Padé approximant but rather with a simple third order polynomial. Also for this reason only low-energy vib-rot levels could be calculated. In total the line list computed contains 14 401, 34 801, 35 471, and 592 lines for SiO, CO, CS, and SiS, respectively.

Kurucz (1991) has recently published an overview of his molecular and atomic opacity data. Although his late work has mainly been concentrated on computations of atomic line strengths, his list is the most complete for diatomic molecules, in the sense that it includes the biggest number of lines. Frequency, gf-value, and excitation energy for a total of 15 million lines from 11 different diatomic molecules of astrophysical interest have been computed. Of these more than half are from the various electronic systems of TiO. Among the other molecules (which are all diatomics), there are 3.5 million lines of the electronic system of C_2, 1.7 million lines from SiO, 1.6 million lines from the blue and red systems of 4 isotopes of CN, and half a million lines from the vibration-rotation bands of CO. The line list is offered on VAX backup tapes, and it is announced to be soon available to the community also on CD-ROMs, which is definitely a big advance in connection with such vast amounts of data. The basic philosophy in Kurucz's line list is to include as many empirical data as possible, and to supplement with computed or estimated data where experimental data do not exist. The computational method is to a certain extent identical to the one described above; but whereas Chackerian and collaborators chose the policy of limiting their computations to the part of the dipole moment function where they estimated the uncertainty to be within a certain limit, it has been the policy of Kurucz to extend the computations toward the dissociation energy to ensure as great a number of lines as possible, but of course with low accuracy for the weak lines. It should be very valuable, but it is a difficult task to compare some of the weakest bands and lines from this extensive data library with observed frequencies and intensities.

Querci et al. (1974) compiled one of the first extensive lists of molecular data for the three diatomic molecules CN, C_2, and CO. The list contains a total of one million lines from various isotopes of these molecules and is available on tape from F. Querci on request. The three molecules are listed together in frequency order, giving for each line an identification of the molecule and isotope, the gf-value and the excitation energy of the lower energy level (but no identification of the lines in the form of, e.g. quantum numbers). The method uses the assumption of an r-centroid describing the relative f-values of the different vibrational transitions within an electronic system, adjusting to measured f-values where existing.

Sharp (1984) has computed a substantial amount of line data for electronic transitions in diatomic molecules. The method used is an advancement on the classical harmonic oscillator calculation, where the potential is treated analytically as a Morse potential function. Franck-Condon factors and r-centroids were computed and listed for C_2, CN, CH, CO, and SiO, and they can be useful tools to predict the general trends of band strengths with vibrational quantum numbers where more detailed computations do not exist. A similar computation was performed to predict the hot-band intensities of the observed bands of HCN and C_2H_2, and line lists for CH, C_2, MgH, and SH were implemented in the oxygen-rich red giant model atmospheres by Brown et al. (1989).

Littleton and Davis (1985) measured f-values for bands from ZrO and YO by use of a high-temperature furnace and the Fourier transform Spectrometer at NSO, Kitt Peak. In a preceding analysis, dipole moment surface and line position results from the analysis were used to construct line data also for the lines not measured, from which opacities were then computed. The data involve full integration of the

theoretical wavefunction of all transitions up to the weakest observed. These data have never been published or even used by the authors, but they are nevertheless already at the disposal of the community on request to J.E. Littleton. Approximately 331 700 lines from the ZrO system and 1 200 lines from the YO system were compiled.

For a number of molecular bands, the band strength may be well known, yet the intensity of the computed synthetic bands based on model atmospheres does not match the observed bands in real stars. This may have many explanations (which may be different from case to case). Most often we will attribute it to insufficient model construction, because the physical input to the computation of the cooler stars, in particular, is generally known to be uncertain. This includes the known incompleteness of the used molecular opacities, as well as the lack of knowledge about when photo-chemical processes may be significant, in which parameter range NLTE effects may be of importance, the magnitude of sphericity and inhomogeneity effects, and (particularly for variable stars) the role of mechanical energy pumping from the bottom of the atmosphere. Even if the model atmospheres were correct, we would also fear that we were not matching the computed and observed basic parameters correctly, and hence we could be comparing slightly wrong models with the stars we wanted to analyse. The latter is not only due to uncertainty in the observed parameters (of which gravity traditionally causes the greatest problem for the late-type stars), but we could also reasonably question, for example, the temperature scale used over a certain range in observed colors. Brett (1990) took the consequence of the many uncertain parameters, and introduced the concept of astrophysical oscillator strengths; i.e. the oscillator strengths that force the synthetic spectra of a given model atmosphere to match the observed band intensity of a given star. The ratio between accepted oscillator strengths and astrophysical oscillator strengths is a good measure of the total uncertainty in our knowledge of everything that goes into the construction of the model atmosphere and synthetic spectrum, and it can therefore be a guide to where to join forces to improve physical knowledge. More important is nevertheless the ability to use astrophysical oscillator strengths to estimate the ratio between the strength of bands known from laboratory (or theoretical) studies to the strength of bands unmeasured in the laboratory. Brett (1990) estimated in this way the strength of the lines in the poorly studied TiOϵ system and in the A-X and B-X systems of VO, i.e. by comparing their astrophysical strength with the astrophysical strength of the better studied δ-system of TiO. For VO these are the only line data that exist, and they are in principle available from Brett although they are not for the moment arranged in the form of an easily readable line list.

Preferentially all bands should, of course, be well studied both theoretically and in the laboratory. In that case every possible mismatch between synthetic and observed band intensities could be attributed to other reasons, and we would have a better chance to learn about the astrophysics of the stars. For a band system to be well studied we should be sure that the strongest bands are well determined in the laboratory; that the complete set of lines (including all weak lines) has been calculated properly; that a reasonable number of very weak lines has been tested against laboratory experiments to assure that the computations are sufficiently accurate to the highest energies; and finally that the temperature dependence of the calculated absorption coefficient is correct. All this is unfortunately not fulfilled for any of the molecules of astrophysical interest. For most of the molecules in question the computations match well the strongest bands, and these are well determined from laboratory experiments. Nevertheless, there are still considerable problems in determining the absolute strength of the strongest bands for some of the radicals; e.g. CN and C_3. The dependence of the overall absorption coefficient on temperature has only been measured in the laboratory for water vapor (Ludwig et al. 1973). Comparison between computed and measured strengths of very weak bands has only been performed for HCN (Smith et al. 1987). A completeness study has only been published for CN (Jørgensen and Larsson 1990). For the latter study the strength of all rotational lines in the A-X ("the red") system was computed individually by integrating the product of the wave function of the upper and lower state up to the dissociation energy. The completeness was estimated, for all relevant temperatures, by summarizing the Boltzmann factor of all the (lower) energy levels considered in the computation and assuring that their sum was more than 99% of the theoretical partition function. The total line list contains more than 3 million lines from 3 isotopes of CN, and it is available from the author on request. The computed frequencies of the strongest lines are accurate to within a fraction of a Doppler width, and the frequencies of the weakest lines

that have laboratory-measured counterparts are accurate to within about 2 cm^{-1}. In a collaboration with N. Grevesse and J. Sauval, we are improving the weak line intensities and frequencies by comparing with their results from solar satellite spectra. The B-X ("the blue") system will also be included in a future version. We have computed similar lists for the CH and HCN molecules, and the results for other molecules will also be available in the future, including the opacity from H_2O and C_3. The completeness of the opacity obtained by including all the weak transitions will affect the synthetic spectra in one or both of two ways. If the weak lines are formed in the part of the spectral interval close to the Planck maximum of the star of interest, the model atmosphere will expand, and the bands of the molecule in question will most likely decrease in intensity due to the decrease in partial pressure following the expansion. If the weak lines fall outside the radiation maximum (e.g. the weak CN bands in cool stars), the model structure will only change insignificantly, but the synthetic spectrum will then change significantly due to the uncompensated (in structure) effect of an increasing "veil" of weak lines.

III. H_2O

H_2O was the first polyatomic molecule to be included in a stellar atmosphere calculation (and for 15 years the only one). The absorption coefficient used in all astrophysical computations so far has been based on the work of Auman (1967) and/or the measurements of Ludwig et al. (1967, 1973). Auman's idea was to collect the laboratory data (band center frequency, molecular constants, and integrated band strength) that were available at the time (i.e. data for 41 vibrational transitions). From these data he estimated the intensity and frequency of the corresponding hot bands and a few difference bands, and distributed them onto line intensities which were then sampled into harmonic and straight mean absorption coefficients in intervals of 100 cm^{-1}. These were later used, either directly or with slight modifications, to construct model atmospheres by, for instance Auman (1969), Alexander and Johnson (1972), Johnson et al. (1980), and Brett (1989). The idea of Ludwig and collaborators was to measure directly the straight mean absorption coefficient by use of an advanced laboratory equipment with long pathlength, coupled with the ability to increase the temperature up to 3000 K such that the temperature conditions in stellar atmospheres and other high-temperature systems could be simulated. The result was likewise a straight mean absorption coefficient over intervals of 100 cm^{-1}. Compared to Auman's data, Ludwig's measurements had the advantage of including all combination and hot bands and with the correct temperature dependence. This kind of data would also be extremely valuable to have for other molecules, but so far they exist only for water. Ludwig's work was used, for example by Tsuji (1971, 1976), Brown et al. (1989), and Plez et al. (1991). The disadvantage of Ludwig's method is that individual lines are not identifiable, and it therefore gives no direct freedom for the choice of line profile and sampling method. (The different sampling methods in use have been summarized by Jørgensen elsewhere in this volume.) Alexander et al. (1989) developed a statistical method to distribute the measured mean absorption coefficient into lines, and thereby demonstrated qualitatively the enormous importance of how the data are sampled. A tape with about 4.5 million lines of the H_2O absorption system was generated, which is now the most complete data on the absorption coefficient of H_2O that is available for astrophysical purposes, and it is offered to the community on request to D.R. Alexander. The data were later used by Brown et al. (1989) to compute model atmospheres, and Plez et al. (1991) used a similar method in constructing their models. A test on the quality of the statistical approach was done by Brown et al. by re-calculating the straight mean absorption coefficient from the line list. For temperatures between 2000 and 3000 K, the agreement with Ludwig's measured absorption coefficient was found to be within a factor of two in the whole spectral interval and in most intervals considerably better. As a nature of the statistical method it is obviously not possible to compare individual lines or bands with observations. Another drawback of any statistical approach is that it has to necessarily introduce a somewhat arbitrary assumption about the number of lines. In principle the water molecule has of the order of 10^9 lines up to J=100, but most of these lines are very weak and will never be observed individually, neither in stars nor in laboratory experiments even at high temperature. How important such lines are for the computed atmospheric model structure and synthetic spectra, and how important the detailed frequency and intensity distribution

of individual bands are, is unfortunately very difficult to quantify before a complete list of all lines has been generated. This can only be done *ab initio* and is a very CPU and disk-space demanding task, if it is to be done to any reasonable level of accuracy.

In quantum mechanical computations of the position and strength of lines and bands, the potential energy as well as the dipole moment are usually computed as functions of the nuclear configurations. The positions of the nuclei are varied to cover the whole stretching- and bending-configuration space that the molecule can span during its vibrational motion. For a diatomic molecule, the possible configurations are represented simply by the different possible nuclear distances along a straight line. For a triatomic molecule, both of the two stretching coordinates as well as the bending of the molecule can vary independently. Whereas the nuclear variation in a diatomic molecule is one dimensional, it is three dimensional in a triatomic molecule. If the computation of the potential energy and the dipole moment in a diatomic molecule is well described by the value in, for instance, 10 points along the internuclear separation, 1000 points would be necessary in a corresponding triatomic computation, and the computation would generally be more cumbersome in each configuration due to the bigger number of unpaired electrons that would be involved in the energy and dipole moment of the given configuration. A typical computing time would be of the order a few CPU hours per configuration on a large scalar computer. The energy and dipole moment for each nuclear configuration are calculated iteratively by varying the electron configuration until a self-consistent result is obtained. This is called the SCF method, and all quantum mechanical methods are based on this principle; but a great number of different numerical approximations are in use and a variety of different levels of sophistication have been applied. A method that has been applied to the computation of intensity and band frequencies for several molecules of astrophysical interest is the so-called complete active space self-consistent field (CASSCF) method, described by Siegbahn et al. (1980, 1981). A central parameter in all methods is the number of basis functions used to describe the wavefunction of the electrons. The greater the number of applied functions, the more accurate is the description, but computing time and the necessary temporary disk storage increase rapidly with increasing size of the basis function set. A good, but storage and time consuming, basis set for most molecules is the natural atomic orbital (NAO) set given by Almlöf and Taylor (1987) and Widmark et al. (1990). A small, but for many modern purposes inaccurate, basis set is given by van Duijneveldt (1970). Basis sets used in practice are often truncations from the NAO set or expansions from van Duijneveldt's set.

When the energy and dipole moment are known for a sufficient number of configurations, an analytical expansion must be determined in order to make it possible to solve the Hamiltonian and to determine the eigenfunctions. This can also be done in a variety of ways. The most commonly used method is to express the potential energy as a polynomial in vibrational coordinate displacements and the vibrational wavefunctions as linear combinations of harmonic oscillator wavefunctions. The basic assumption here is that the molecule, to a first approximation, can be viewed as a set of non-interacting harmonic oscillators with amplitudes that are small compared to the dimension of the molecule. To a second order, anharmonicity terms are then introduced. In many real molecules the anharmonicity terms are nevertheless big, and the approximation is therefore not a good description particularly for the higher vibrational levels. This is reflected spectroscopically in the fact that new molecular constants are needed for each vibrational level in order to get a good description of the rotational structure. The constants are then rather a mathematical device to predict line positions. The connection between experimentally determined molecular constants and the physically relevant potential energy is then no longer obvious, and an introduction of observed quantities into the *ab initio* calculations is hindered. In a newly developed and very promising approach, the potential is expressed as a sum of a term that corresponds to a rigidly bending molecule and an expansion in products of functions of the cosine of the bending angle and Morse-type stretching functions. The method has been named MORBID, for Morse oscillator rigid bender internal dynamics, and it has been described by Jensen (1988a,b) who has also tested the difference in the computed energy levels by fitting both a MORBID type potential and a polynomial type potential to the same *ab initio* calculations. The MORBID type potential was found to give much superior results for the stretching vibration frequencies and results similar to the polynomial fit for bending vibrations. Jensen (1989) has, by use of 19 MORBID molecular constants, fitted the potential energy of H_2O to 103 experimentally determined vibrational energy levels and rotational spacings for $J \leq 2$ where available. The resulting eigenstates

are in much closer agreement with observed levels than previously reported computations, and the standard deviation between 550 measured and calculated line frequencies is 0.63 cm^{-1}. Jensen, Jørgensen and Sørensen (1991; in preparation) used this potential—together with values of the dipole moment computed by use of the CASSFC theory for 300 nuclear configurations of the water molecule—to compute the frequency and strength of all 85 000 possible vibrational transitions between vibrational eigenstates up to 30 000 cm^{-1}. It is planned to compute an extensive OS (opacity sampling) line list from these data, which can be used for model atmosphere computations as well as for low resolution synthetic spectrum computations, and also a set of ODFs (opacity distribution functions) will be computed and offered to the community (on request to the author) as a SCAN-H_2O tape (as for CN and other molecules). The full line list is expected to contain 10^9 lines and will not be practically transportable with present-day magnetic tape storage capacities.

IV. HCN, C_2H_2, AND C_3

Jørgensen et al. (1985) computed the absorption coefficient of HCN using a method very similar to the quantum mechanical method described above for the water molecule, but used a polynomial fit to the dipole moment and potential energy surface and a substantially smaller basis set than the one later used for H_2O (due to the more limited general computer capacity available then). The results were later compared to observations (Smith et al. 1987) of bands as weak as 10^8 times weaker than the fundamental. Assignment problems of the computed bands made it difficult to compare with these very weak observed bands individually, but it was concluded that even the weakest part of the computed integrated absorption coefficient agreed with the observations to within a factor of 3. The intensity and frequency of the strong bands agree with observations to within a few percent. With the improved technique used, described above in connection with *ab initio* computations for the water molecule, it is likely that the individual weak bands could have been identified from the computations, and that a considerably better absorption coefficient for the weak bands could have been computed. Such a computation is one of the future projects we are considering. It is worth noting that inclusion of the weak bands only changes the absorption coefficient, integrated over the whole spectrum, insignificantly (typically by a few percent); but it can change the stellar model atmosphere structure by several orders of magnitude (Eriksson et al. 1984) due to the relatively big change of the (still weak) absorption in selected intervals of the spectrum, although these bands may not be observable individually in the spectrum (Jørgensen 1990). This is what makes the completeness and high accuracy of the computations so important. It has already been noted by Tsuji (1984) that the inclusion of only the observed bands of HCN and the hot bands (estimated by the VAEBM model) did not affect the structure of the model atmospheres appreciably. Later Sharp (1984; and ref. in Brown et al. 1989) recomputed the hot bands of the observed HCN bands in a more refined treatment than Tsuji's, but the results have not yet been tested in model atmosphere constructions.

The absorption coefficient of C_3 in its electronic ground state (i.e. the infrared vibration-rotation system) was computed by Jørgensen et al. (1989) using a method similar to the one used for HCN. The absorption coefficient of C_2H_2 has not been computed *ab initio*, but only estimated from a semiempirical method where unmeasured combination bands are assigned a band strength according to the change in the vibrational quantum number between the upper and lower vibrational levels; on the other hand, measured bands were included with their measured band strength, and hot bands were computed in the harmonic approximation (Jørgensen 1982; unpublished work). Even though the absorption coefficient computed in this way is the most complete computation existing for C_2H_2, it must still be regarded as preliminary, and improvement is urgently needed particularly for the red and photographic infrared part of the spectrum. For all the three molecules the computed integrated band strengths were distributed onto lines according to the formulas for linear molecules, and the lines collected in Opacity Distribution Functions (ODFs) or according to the Opacity Sampling (OS) technique before being included in model atmosphere computations. The band strength represents the cumbersome computational part. The line intensities have been re-computed from the band strengths several times, and are therefore not exactly the same in all the models that have been published with the use of these opacities; but approximately 10 million lines are usually included for each of the three

molecules. Also the treatment of degeneracy has been improved since the publication of the first models. Of the three molecules, HCN has been found to be of highest importance for stars with C/O close to one, whereas C_3 and C_2H_2 increase in importance when the C/O ratio increases and for respectively warmer and cooler models.

V. ACETYLENIC RADICALS (C_nH, n=2,3,4,5,6,...)

Ethynyl, C_2H, is the smallest of the acetylenic radicals and therefore the most likely to be found in stellar environments. Although it has not yet been identified in a line-by-line study in the photosphere of any star, it is predicted to have a high partial pressure in the atmosphere of cool carbon stars. It was identified in interstellar space nearly 20 years ago (Tucker et al. 1974), and it is found to be surprisingly abundant in molecular clouds and in dense carbon-rich circumstellar envelopes. In IRC+10216, microwave lines of this molecule have been recently detected by Truong-Bach et al. (1987; and references therein), and infrared lines of the $A^2\Pi \leftarrow X^2\Sigma^+$ system have been observed by Keady and Hinkle (1988) in the same object. Keady and Hinkle identified 29 lines of the 110-000 band at 4011 cm^{-1} and the 012-000 band at 4108 cm^{-1}. The analysis pointed to a rotational temperature of 19 K and a velocity relative to the star of -14.6 ± 1 $km\,s^{-1}$. The molecule is only identified at large distances of the star, and it is assumed to form from photodissociation of C_2H_2 at distances of the order 1000 R_*. Cernicharo et al. (1987a,b) detected rotational transitions of C_3H, C_5H and C_6H in the microwave spectrum of IRC+10216 and determined rotational temperatures of 14, 20 and 30 K, respectively.

Goebel et al. (1983) suggested the identification $A^2\Pi(0,0,0) \leftarrow X^2\Sigma^+(0,0,0)$ of C_2H for a band at 2.9 μm in the photospheric spectrum of the R-type carbon star HD 19557. The spectrum was based on low resolution CVF scans with the instruments on board the Kuiper Airborne Observatory. Observations, as well as the assignments of laboratory measured lines of this molecule, are non-trivial. Their study was therefore based on a simplified *ab initio* computation where interactions between the different electronic levels were ignored, a limited number of stretching and bending configurations were calculated, and a product of three Morse potentials was fitted to the results. Unfortunately, results from different computations of the minimum energy, T_e, of the potential curve representing the $A^2\Pi$ state, differ as much as from 4030 cm^{-1} (=2.5 μm; Shih et al. 1979) to 2000 cm^{-1} (=5.0 μm; Fogarasi et al. 1983). A value of 3417 cm^{-1} (2.9 μm) gave a good fit to the position of the unidentified feature in the spectrum of HD 19557, and it is obviously in agreement with *ab initio* results as well as with laboratory measurements. Although newer *ab initio* computations point to a value of T_e between 2.7 μm (Kraemer et al. 1986) and 3.0 μm (Thümmel et al. 1989), even this range gives an unsatisfactory wide margin on the possible position of the $A^2\Pi(0,0,0) \leftarrow X^2\Sigma^+(0,0,0)$ band. The resolution in the observations by Goebel et al. was not high enough to permit identification of individual rotational lines. The existence of C_2H bands in HD 19557, where no 3 μm band (from HCN and/or C_2H_2) and no 5 μm band (from C_3) are present, would imply C_2H to be present in stars whose temperatures were too high for HCN, C_2H_2, and C_3 to exist. We have calculated a number of carbon star models with different C/O ratios, metallicities, T_{eff} 's, gravities, and masses, but we find no evidence for such a behaviour in our models; on the contrary we find that the partial pressure of C_2H is always exceeded by either HCN (most models) or C_3 (models with high T_{eff} and C/O). It must be stressed that our models do not include C_2H in the opacity (due to the lack of molecular data), but generally the inclusion of the opacity of a molecule will not increase, but rather decrease, the partial pressure of this species. HCN, C_2H_2, as well as C_3 are all included in our opacity and model atmosphere computations (e.g. Jørgensen et al. 1989).

In a series of very detailed quantum mechanical investigations of the structure of C_2H (Reimers et al. 1985, Kraemer et al. 1986, Tümmel et al. 1989, Perić et al. 1990a,b), the authors promote the idea that the difficulties in the earlier theoretical investigations and in the interpretation of the observations are due to a unique structure of the electronic levels of this molecule. The three lowest lying levels in a molecule belonging to the C_s point group are called $1^2A'$, $2^2A'$ and $1^2A''$, in analogy with the naming B, A, X in the description of diatomics or other linear molecules. Normally the three electronic states will be well separated, with $1^2A'$ and $2^2A'$ (Π) being above the ground level $1^2A''$ (Σ). In C_2H the authors, nevertheless, find that all three

levels mix, in the sense that the potentials for the three levels cross one another even for what corresponds to a relatively small vibrational (C-C) stretching displacement. This gives rise to a very complex electronic band structure, without the simple sequence of well separated vibrational bands that we are used to from the electronic systems of CN, C_2, and TiO. In particular, the lines from the vib-rot bands are therefore expected to appear mixed with the lines from the electronic transition in the same regions of the spectrum.

The theoretical results of Kraemer et al., in particular, and the results of Perić et al. are in good agreement with recently available experimental results, and they strongly disagree with a more straightforward interpretation of the positions and the form of the electronic potentials (and hence of the observed data) given by Fogarasi et al. (1983). From an experimental point of view, there has been a long-standing debate about the possible assignment to various observed bands. The most recent and detailed experiments suggest the ν_3 (C-C stretching) fundamental to be at 1840.57 cm^{-1} (5.4 μm; Kanamori et al. 1987), the ν_2 (bending) fundamental to be at $\approx$ 260 cm^{-1} (38.5 μm; Shepherd and Graham 1987), and the ν_1 (C-H stretching) fundamental to be at 3611 cm^{-1} (2.7 μm; Jacox and Olson 1987, although these authors discuss the possibility of the band center rather being at values as low as 3000 cm^{-1} = 3.3 μm). The difficult region of mingled vib-rot and electronic bands around 3 μm was recently discussed by Yan et al. (1987). Theoretically, for example Perić et al. (1990b) obtains $(\nu_1, \nu_2, \nu_3)_\Sigma$ = (3550, 370, 2000) cm^{-1} in reasonable agreement with the observed values.

Propynylidyne, C_3H, is predicted to have a partial pressure about one-tenth that of C_2H in our cool carbon star model atmospheres, which still makes it one of the most abundant molecules in the upper photosphere. But only very little is known about this molecule, and all model atmosphere constructions so far have therefore assumed that it is 100% transparent as assumed also for C_2H. Jacox and Milligan (1974) identified the antisymmetric C-C stretching mode of C_3H to be at 1824.8 cm^{-1} (5.48μm), but not before 1990 were the symmetric C-C stretching fundamental (at 1159.7 cm^{-1} = 8.62μm) and the C-H stretching fundamental (at 3238.0 cm^{-1} = 3.09μm) frequencies proposed (Huang and Graham 1990). The geometry was predicted by Green (1980). In circumstellar envelopes and molecular clouds (particularly IRC +10216 and the cool dust cloud TMC-1), C_3H has been identified from its microwave spectrum (e.g. Johansson et al. 1984, Thaddeus et al. 1985a) and compared to laboratory studies (e.g. Gottlieb et al. 1985, Yamamoto et al. 1987, Yamamoto and Saito 1990). Yamamoto et al. (1987) discovered that also the cyclic form of the C_3H molecule, c-C_3H, can be produced in the laboratory, and they identified it in TMC-1 (c-C_3H is easily distinguishable from the linear, l-C_3H, by its hyperfine structure). The c-C_3H was searched for in IRC +10216 as well as in Cas A, but it was not identified. The c-C_3H is slightly more abundant than the l-C_3H in TMC-1 (6/5), but [c-C_3H/l-C_3H]$\leq$0.2 in IRC +10216. This is similar to [HNC]/[HCN] being 1.5 in TMC-1 (Irvine and Schloerb 1984) but $\leq$ 0.01 in IRC +10216 (Olofsson et al. 1982). Mangum and Wootten (1990) identified the $c-C_3H$ molecule in 13 out of 19 searched interstellar clouds. They found $[c-C_3H]$:$[C_3H_2]$ = 1:10 within a factor of two in all clouds (independent of temperature, etc.), and therefore concluded that the two molecules must have a common precursor, $C_3H_3^+$, which most likely indicates that none of these molecules comes from the stellar photosphere; but they are formed by photo-dissociation in circumstellar envelopes or in the interstellar medium. The only other carbon-ring molecule that has until now been identified in space is cyclopropenylidyne, C_3H_2 (Thaddeus et al. 1985b).

Butadiynyl, C_4H, is not presented in our equilibrium computations, but we expect its partial pressure to be at least an order of magnitude below that of C_3H and therefore of only marginal importance for the structure and opacity of even very cool N-type stars although photo-dissociation processes might bring its partial pressure significantly up, as seen in circumstellar envelopes where it is as abundant as C_2H. Shen et al. (1990) identified the C$\equiv$C ν_2 mode at 2083.9 cm^{-1} (=4.80μm) and the C-H ν_1 mode at 3307.4 cm^{-1} (=3.02μm), and they confirmed the only prior known fundamental vibration mode: the C$\equiv$C ν_3 mode at 2060.6 cm^{-1} (=4.85μm). Other vibration-rotation bands apart from these are not known. C_5H has been detected in interstellar space by Cernicharo et al. (1986) and C_6H by Suzuki et al. (1986). An extensive survey of available data on the small carbon and hydrogen containing molecules has recently been compiled by Jacox (1988).

VI. POLYYNES, BENZENE, PAH, SOOT, AND CARBON CLUSTERS

The prediction of the existence of acetylenic radicals in the photosphere of cool stars—and its identification in circumstellar envelopes (CSE) and in the interstellar medium (ISM) in both linear and cyclic form—opens up the exciting question of the existence of even more complex molecules in the upper photosphere of cool stars; particularly in carbon-rich stars due to the complexity of the carbon chemistry. If such molecules form in greater amounts, their influence on the opacity will be huge. Frenklach et al. (1989) suggested a scenario where small molecules successively built up more and more complex molecules, including ring-structures, on their way out through the upper layers of carbon-rich red giants, and they eventually become the precursors of the large interstellar grains. The laboratory experiments behind the theory are based on very high pressure compared to the gas pressure existing in carbon stars, and the molecular formation route is therefore basically wrong (including, for example, the formation of CH_4 as in the solar system formation); but as an idea it is certainly interesting, and a search for complex carbon molecules in the upper photosphere of red giants deserves high priority.

The longest carbon chains observed in interstellar space are of the form HC_nN, n=1,3,5,7,9,11,..., (called polyynes) where up to n=11 has been observed. Radio measurements show the chains with additional H-atoms to have significantly lower abundances than the polyynes, which is surprising because of the fact that $(C/H)_\odot = 10^{-4}$. Detection (Guélin and Cernicharo 1991) of the HCCN radical in IRC +10216 (and also in Sgr B2 and Ori A although less abundant) indicates that also the family $HC_{2n}N$, n=1,2,3,..., may be formed in CSE but in smaller amounts than the HC_nN, n=1,3,5,..., molecules. For instance, the ratio HCCCN/HCCN exceeds 100.

It is energetically convenient to bend the linear carbon chains into rings with alternating double and single bonds between the carbon atoms. The smallest possible is C_3, and certainly C_3H_2 has been observed as noted above as well as cyclic C_3H. The most well known carbon-ring is probably benzene, C_6H_6. The carbon ring-structure of benzene can be used to build up infinite, flat, chicken-net-like structures. The molecules thus obtained, with several benzene rings and with hydrogen at the unsaturated edges, are called polycyclic-aromatic-hydrocarbons or PAH. Aromatic refers to the linkage of the form =C−H with a p-orbital out of the molecular plane. Among the most discussed are pyrene (with 4 rings), coronene (with 7 rings; $C_{24}H_{12}$), and ovalene (with 10 rings). None of them has actually been identified in space in terms of a line-by-line identification, but they could play an important role in both interstellar space and as an intermediate step in the formation of dust in stellar atmospheres because of their great stability against photodissociation. Their line profiles are predicted to have a very characteristic form that has not been found in the interstellar lines. (But this can have various other explanations rather than the non-existence of PAHs; see, for instance, Cossart-Magos and Leach 1990.) In stellar environments a similar line profile study has not yet been carried out. Five characteristic infrared nebular emission features at 3.3, 6.2, 7.7, 8.6 and 11.3 μm are suspected to be due to PAHs (see, e.g. Léger and Puget 1984, Jourdain de Muizon et al. 1990). Only the small and medium-sized neutral molecules (up to coronene) have been studied in the laboratory, and none of the ions has been studied so far. Particularly the cations are expected to play an important role in interstellar space. Several recent reviews have been devoted to PAHs, particularly the proceedings by Léger et al. (1987) and Bussoletti and Strazzulla (1991) and the Annual Reviews paper by Puget and Léger (1989).

Geometrically, one can bend a layer of hexagons (like the benzene rings) by imposing impurities of 12 pentagons to form stable closed structures (called fullerenes) with 20, 24, 28, 32, 50, 60, 70, ... carbon atoms. Mass spectra of laser experiments (Kroto et al. 1985, Zhang et al. 1986) show the fragments or nucleation products to have these magic numbers, in support of the hexagon-pentagon hypothesis. Krätschmer et al. (1990) have extracted C_{60} (and name it fullerite in the solid form as opposed to fullerene in the gas phase) from soot produced by evaporating graphite electrodes in $\approx$ 100 torr helium atmosphere. Enough fullerite can be produced in this way to perform IR, UV, Raman, and mass spectroscopy, electron and X-ray diffraction, and NMR measurements. The IR spectra show four clear lines at 7.0, 8.45, 17.3 and 18.9 μm. In the UV, broad peaks at 2160, 2640, and 3390 Å dominate the spectra. Wragg et al. (1990) used scanning tunnelling microscopy to actually photograph the single C_{60} and C_{70} "soccer balls" in the same solid extracts. They show

up as 10-Å spherical molecules that are packed together to form microcrystalline particles of size 100 Å that resemble raspberries. This was the first direct evidence that the carbon clusters that had earlier been identified in mass spectroscopy to have the mass of 60 carbon atoms were actually of spherical form, as predicted by the theory of the fullerene-form.

Whether or not these polyhedral carbon clusters are responsible for the interstellar bands, and therefore likely to form in cool stellar atmospheres, is an outstanding question. Krätschmer et al. (1990) found no obvious matches between the known interstellar features and the spectra of the produced (solid) fullerite. This may not be a surprise, since the clusters may be in the gas phase (fullerene) in the ISM (and definitely in CSE and stellar photospheres). C_{60}-fullerene has no permanent dipole moment and therefore no rotational spectrum, but among its many possible vibrational frequencies, four are infrared allowed (by symmetry) and (only) one UV-visual electronic transition is allowed. The theoretical UV spectrum has been discussed by Larsson et al. (1987), and the vibrational modes by, for example, Weeks and Harter (1989). Heath et al. (1987) observed the gas phase UV transition as an only 50 Å wide band at 3860 Å, in agreement with the theoretical computations of Larsson et al. (1987). In astrophysical environments, where hydrogen is nearly always very abundant, some of the pentagons may be substituted with hydrogen bonds, and the spectrum of the "impure" fullerenes we may find in stellar and interstellar environment may therefore be different from even the gas-phase pure fullerenes. Furthermore, there are indications that at least in the ISM the C_{60} will be transformed into C_{60}^+, which has many more allowed electronic transitions than neutral C_{60} because of the lower symmetry, but its bands have not yet been analysed in the laboratory.

Léger et al. (1988) list the pros and cons in the debate on whether PAH or carbon clusters are responsible for the unidentified diffuse interstellar bands. The main reasons to believe that C_{60} should be abundant in the ISM and in the upper photosphere of cool carbon stars are the ease of formation of the carbon clusters and their unique stability compared to most other molecules; and C_{60}^+ is indeed found to be the most abundant ion in, for example, sooting flames (Gerhardt et al. 1987). Zhang et al. (1986) found that the neutral fullerene was completely unreactive, even in the presence of such reactive gasses as O_2, NH_3 and NO (Curl and Smalley 1988), and Weiss et al. (1988) found that also C_{60}^+ was completely inert. Lewis et al. (1987) searched for C_{60} clusters in meteorites known to contain interstellar grains, but they did not find any. In interstellar space UV radiation may ionize the clusters, and laboratory experiments show that irradiation with UV light will cause the smaller fullerenes to lose C_3 molecules (Geusic et al. 1986) whereas fullerenes bigger than C_{32}^+ lose C_2 and C (O'Brien et al. 1988). C_{32}^+ itself will fragment into pieces in the 10- to 19-atom range. The C_{60} fullerene is of course particularly hard to photo-dissociate. There are therefore many arguments in favor and against the possible existence of complex, big carbon molecules in the photosphere of carbon stars and in the interstellar medium; but this exciting new field is so rapidly evolving that it is certainly very interesting to follow, and it may turn out to have very strong implications in stellar as well as interstellar astronomy.

VII. CONCLUSIONS

Research in molecular opacities has mainly been concentrated on diatomic molecules; huge compilations of line lists exist although relatively little is known about the accuracy and completeness of these lists, and no comparison of the compilations has been performed in the few cases where two or more independent line lists exist. Of the polyatomic molecules, opacities of (only) H_2O, HCN, C_3, and C_2H_2 have been computed, and their effects on the stellar structure of cool stars are known to be substantial. Of the smaller polyatomic molecules, where important work is in progress, C_2H has particularly proven very difficult to calculate, and even though this molecule is predicted to be very abundant in cool stars, it has never been identified in the photospheric spectrum. Photo-chemical processes are likely to be important in the upper photosphere of cool stars, and valuable knowledge can be gained by looking at results for CSE and the ISM. Here very complex molecules are predicted to form and a great number have been observed. Whether these play an important role for the opacity of the uppermost layers of the stellar photosphere is still to be explored, but their effect may well completely change our understanding of the stellar atmospheric structure.

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