OPTICAL OBSERVATIONS OF INTERSTELLAR MOLECULES

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ABSTRACT

Recent observational data are summarized on molecular species in diffuse interstellar clouds, and a comprehensive list of all species detected or sought is included. The discussion is focussed on the use of molecular observations to determine physical conditions in clouds, and on important species which provide constraints on cloud chemistry models. Directions for new research are suggested, including intensive work on the unidentified diffuse bands, which may have a molecular origin.

I. INTRODUCTION

This reviewer was asked to summarize current knowledge of molecular species and characteristics in hot diffuse clouds. The title which has been adopted reflects the fact that, to date, observations of molecules in diffuse clouds have been carried out almost exclusively by optical measurements of absorption lines in the spectra of background stars. There have been cases of radio detections of molecular emission lines arising in diffuse clouds, but these detections generally require very long integration times which are only infrequently devoted to this purpose. Hence the present review will be concentrated upon the optical absorption-line data.

The first detections and identifications of molecular species in diffuse clouds (or in any clouds, for that matter), were achieved before 1940, when lines of CH, CH^+, and CN were found in the spectra of reddened stars (Adams 1941; Adams and Dunham 1937). With the possible exceptions of the unidentified carriers of the diffuse interstellar bands (about which more later), these three diatomics remained the only molecules detected through traditional ground-based spectroscopic techniques until well into the 1970's. By the 1960's, ultraviolet spectroscopy of astronomical objects became feasible, at first with sounding rocket instruments, and nearly ten years ago H_2 was detected by Carruthers (1970). Later rocket experiments succeeded

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in measuring absorption lines of CO (Smith and Stecher, 1971). Since the launch of Copernicus in August 1972, a considerable renewal of activity has occurred, both in ultraviolet and in visible-wavelength observations of molecules. New species such as OH, C_2, and possibly H_2O, have been detected and rigorous searches for others have been carried out. Along with the observations, theoretical work on chemical reactions in interstellar clouds has provided increasingly detailed understandings of results already in, and has issued numerous challenges for new observations to be attempted.

With this tradition of close interaction between observation and theory in mind, the present review is designed to acquaint scientists in related areas with the current state of knowledge of molecular species in diffuse clouds (where the chemistry is far simpler than that in the dark clouds studied by the radio observers) and to challenge not only the theorist but also the laboratory spectroscopist, since one of the major requirements for progress in this field is the accumulation of basic data on the species sought.

II. OBSERVATIONAL RESULTS

In this section are briefly described the results of optical spectroscopic observations of molecular species. Table 1 lists all those known to the author to have been detected or sought. The discussion following will be concentrated on a few of these, singled out for their significance as probes of physical conditions or tests of chemical models. The table gives references to recent observations of all the listed species. No detailed description of observational instruments or techniques will be included here; this information may be obtained from the original references.

a. Indicators of Physical Conditions

Molecular observations can be useful to the student of the nature of interstellar clouds as well as to the cloud chemist. Such parameters as kinetic temperature, density, cosmic ray ionization rate, and radiation field intensity all can be derived from observations of molecular species.

Diffuse cloud kinetic temperatures are presumed equal to the rotational excitation temperature indicated by the ratio of hydrogen molecules in the first rotational excited state and the ground state, since H_2 is a homonuclear molecule with no allowed radiative dipole transitions between adjacent rotational states (Dalgarno, Black, and Weisheit, 1973). Measurements of this ratio in diffuse clouds have revealed values of T_{kin} ranging from about 40K to 100K or more (e.g., Spitzer and Cochran 1973; Savage et. al. 1977). Another homonuclear molecule with potential to be an indicator of cloud temperatures is C_2, recently detected by several observers (Lutz and Souza 1977; Snow 1978; Hobbs 1979; Chaffee et. al. 1979). For the ζ Ophiuchi cloud, Snow (1978) found $T_{kin} \lesssim 16K$ from ultraviolet observations with Coper-

Table 1. Interstellar Molecules Observed in Optical Absorption

Species	Wavelength	Star	$N(cm^{-2})$	N/N_H	Reference[+]
H_2	912-1108	ζ Oph	4.47×10^{20}	0.32	13,20
HD	912-1108	ζ Oph	1.58×10^{14}	1.12×10^{-7}	20
C_2	8758	ζ Per	1.2×10^{13}	8.51×10^{-9}	4,8
C_3	4050	ζ Oph	$<2 \times 10^{11} f^{-1}$	-	5
CH	4300	ζ Oph	3.39×10^{13}	2.40×10^{-8}	1,7
CH^+	4232	ζ Oph	1.2×10^{13}	8.51×10^{-9}	22
$^{13}CH^+$	4232	ζ Oph	1.32×10^{11}	9.36×10^{-11}	21,22
CN	3874	ζ Oph	4.79×10^{12}	3.40×10^{-9}	7
CN^+	2181	ξ Per	$<1 \times 10^{12} f^{-1}$	-	9
CO	1088	ζ Oph	1.2×10^{15}		14
^{13}CO	1395	ζ Oph	$<5.62 \times 10^{13}$	$<3.99 \times 10^{-9}$	12
CO^+	4251	ζ Oph	$<5.75 \times 10^{12}$	$<4.08 \times 10^{-9}$	2,7
CS	2577	ζ Oph	$<2.55 \times 10^{13}$	$<1.81 \times 10^{-8}$	17
CH_2	1397	ζ Oph	$<1.56 \times 10^{12} f^{-1}$	-	17
CO_2	1089	ζ Oph	$<2.95 \times 10^{13} f^{-1}$	-	17
NH	3358	o Per	$<7 \times 10^{11}$	$<4.49 \times 10^{-10}$	6
NH^+	2890	ζ Oph	$<1.65 \times 10^{11} f^{-1}$	-	17
N_2	958	δ Sco	$<3.8 \times 10^{12}$	$<2.62 \times 10^{-9}$	11
NO	2262	ξ Per	$<1.70 \times 10^{15}$	$<1.21 \times 10^{-6}$	9
NO^+	1313	ζ Oph	$<1.07 \times 10^{14}$	$<7.59 \times 10^{-8}$	12
OH	1222	ζ Oph	5.24×10^{13}	3.72×10^{-8}	17
O_2	1144	o Per	$<3.47 \times 10^{11} f^{-1}$	-	16
H_2O	1114	ζ Oph	$<2.65 \times 10^{13}$	$<1.88 \times 10^{-8}$	15,19
NaH	3991	ζ Oph	$<1.7 \times 10^{11}$	$<1.21 \times 10^{-9}$	18
MgH	5187	ζ Oph	$<2.2 \times 10^{11}$	$<1.56 \times 10^{-10}$	7,10
MgH^+	2806	ξ Per	$<2 \times 10^{11} f^{-1}$	-	9
AlH	2242	ζ Oph	$<2.56 \times 10^{11} f^{-1}$	-	17
SiH	4119	ζ Oph	$<1.41 \times 10^{12}$	$<1.00 \times 10^{-9}$	7
SiO	1310	ζ Oph	$<3.24 \times 10^{11} f^{-1}$	-	12
SH	1257	o Per	$<1.45 \times 10^{11} f^{-1}$	-	16
HCl	1290	ζ Oph	$<1.29 \times 10^{12}$	$<9.15 \times 10^{-10}$	15,23
CaH	2717	ζ Oph	$<9.34 \times 10^{10} f^{-1}$	-	17

[+]References to Table 1.

1. Black and Dalgarno 1973b
2. Bortolot and Thaddeus 1969
3. Chaffee and Lutz 1977
4. Chaffee et. al. 1979
5. Clegg, Lambert, & Snell 1979
6. Crutcher and Watson 1976b
7. Herbig 1968
8. Hobbs 1979
9. Jenkins et. al. 1973
10. Kirby, Saxon, & Liu 1979
11. Lutz, Owen, & Snow 1979
12. Morton 1975
13. Savage et. al. 1977
14. Smith, Krishna Swamy, & Stecher 1978
15. Smith, Yoshino and Parkinson 1979
16. Snow 1975
17. Snow 1976a
18. Snow and Smith 1977
19. Snow and Smith 1979
20. Spitzer, Drake et. al.
21. Vanden Bout 1972
22. Vanden Bout 1979
23. Wright and Morton 1979

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nicus. Hobbs (1979), utilizing a near-infrared transition, found T_{kin} =78 ± 25K for the cloud towards ζ Persei while Chaffee *et al.* found T_{kin} = 92 ± 10K for the same cloud. The C_2 result for ζ Oph showed a much lower T_{kin} than that found for the same cloud from H_2 measurements, whereas good agreement between the H_2 and C_2 results was found for the ζ Per cloud. It is noteworthy that the detailed models of both clouds by Black and Dalgarno (1977) and by Black, Hartquist, and Dalgarno, (1979) invoke a bi-modal structure, with a cold core and a warmer outer region. Chaffee *et. al.* (1979) show that radiative pumping can affect the rotational distribution in C_2 so that the C_2 data may be in harmony with the values of T_{kin} derived from the H_2 observations.

Cloud densities can be derived from observations of rotational excitation in CO, which is collisionally excited primarily by H_2 molecules in diffuse clouds. Ultraviolet observations of CO molecules with *Copernicus* have resulted in values of $n(H_2)$ ranging from less than 100 cm^{-3} to over 1000 cm^{-3} (Snow 1976b, 1977; Smith, Krishna Swamy, and Stecher 1978; Snow and Jenkins 1979).

The cosmic ray ionization rate can be derived from observations of HD or OH abundances, since the reaction sequences leading to these molecules are initiated by H^+ ions. By observing the abundance of HD or OH, one can infer the equilibrium abundance of H^+, which in turn indicates the cosmic ray ionization rate.

It was noted early in the lifetime of the *Copernicus* satellite that H_2 often shows excess populations of the high rotational levels (i.e., J=4-6) as though a second, higher temperature governed their populations rather than that which controls the low levels. This excess excitation was first reported by Spitzer and Cochran (1973) and Spitzer, Cochran, and Hirshfeld (1974), and subsequently attributed to excess kinetic energy of formation of H_2 molecules as they are liberated from grains (Spitzer and Zweibel 1974). At about the same time, Black and Dalgarno (1973a) suggested that pumping via ultraviolet resonance line absorption was responsible for the high J-level excitation, and later Jura (1975 a, b) was able to use this model to show how radiation field intensities can be derived from observations of the excitations of H_2. The basic idea is that electronic transitions from the ground state via the Lyman and Werner bands leave the molecules in excited vibrational and rotational states of the first excited electronic level. As the molecules return radiatively to the ground state, the equilibrium populations of the high J-levels are determined by the branching coefficients which indicate the relative probabilities of the various paths through the vibration-rotation cascade. By analyzing the high J-level populations, Jura (1975 a, b) and Spitzer and Morton (1976) found radiation field intensities ranging up to 10-15 times the average interstellar radiation field, revealing clouds which are in close proximity to their background stars. The analysis of Spitzer and Morton showed that in several lines of sight, the highly-excited H_2 (inferred to be close to the star) inhabits a

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cloud which has a negative velocity with respect to the star, suggestive of an expanding shell, perhaps produced by a stellar wind or an old supernova. Very recently, Wright and Morton (1979) were able to utilize the observed rotational excitation in HD to derive the radiation field intensity of the main cloud seen towards ζ Ophiuchi, thus determining the cloud's distance from the star. Hence, molecular observations, through their revelations concerning cloud physical conditions, can also indirectly yield information on cloud geometries and kinetics.

b. Molecular Formation and Tests of Chemical Models

Every detection or new upper limit for a molecular species provides useful data on the mechanisms which govern cloud chemistry.

For the diffuse clouds, it now appears likely that most species (excepting H_2) are formed through gas-phase reaction sequences initiated by cosmic ray or UV ionization, followed by charge-exchange and ion-molecule reactions. The alternative process, formation of molecules on grain surfaces, is likely the principal source of H_2 but not of other species, although some workers (e.g., Allen and Robinson 1977 and Pickles and Williams 1977) contend that formation on grains can occur rapidly enough to compete with the gas-phase processes. In this observational review no attempt is made to settle the issue, but results are described which bear on the question.

Evidence favoring the gas-phase formation hypothesis comes in two forms: (1) recent detections, at about the predicted level, of species expected to be abundant under this hypothesis; and (2) failure to detect, despite intensive searches, species expected to be produced efficiently by grain surface formations but not by gas-phase reactions. In the former category fall OH (Crutcher and Watson 1976a; Chaffee and Lutz 1977; Snow 1976a) and C_2 (Souza and Lutz 1977; Lutz and Souza 1977; Snow 1978; Hobbs 1979; Chaffee et al. 1979); in the latter category are NH (Crutcher and Watson 1976 b) and NaH (Snow and Smith 1977

Important tests which have been attempted but are not yet successfully completed include searches for N_2, HCl, and H_2O, all three of which are predicted to have substantial abundances in diffuse clouds, if gas-phase reactions dominate (e.g., Black and Dalgarno 1977). The search for N_2 (Lutz, Owen, and Snow 1979) is hampered by the fact that the most favorable transitions are below 1000A, where it has been feasible to observe only little-reddened stars. In the case of HCl, predicted to be abundant by Jura (1974) and by Dalgarno et. al. (1974), the f-value has just been determined (Smith, Yoshino, and Parkinson, 1979), and the current upper limit (Wright and Morton 1979) is well below the predicted level. The discrepancy between the observation and theory may be too large to be explained by uncertainties in the photoionization rate for ClI, as proposed by Jura and York (1978). The chemistry of HCl is discussed further by Black and Smith (1979).

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The triatomic species H_2O, formed through the same reaction sequence as OH, has been marginally seen (Snow and Smith 1979), at about the 2σ level. In this case the line strength has also just been determined (Smith, Yoshino, and Parkinson 1979) yielding a probable column density for H_2O which is larger than that predicted by Black and Dalgarno (1977). A more solid determination will help establish the value of the branching ratio in the reaction

$$H_3O^+ + e \begin{cases} \rightarrow OH + H_2 \\ \rightarrow H_2O + H, \end{cases}$$

recently estimated (Herbst 1978) to favor OH by about a factor of 10, helping to make H_2O difficult to detect.

An outstanding problem for theories of molecule formation is posed by the large quantities of CH^+ that are observed. Since the reaction

$$C^+ + H_2 \rightarrow CH^+ + H$$

is endothermic by 0.4ev, and the destruction process is very rapid, it is difficult to understand CH^+ abundances in diffuse clouds. Recent suggestions have invoked CH^+ formation in either shock fronts (Elitzur and Watson 1978) or in the warm outer portions of clouds (de Jong 1979), where the necessary energy can be provided. Careful observations of CH^+ velocities in lines of sight known to contain shocked clouds should help test these suggestions.

IV. CHALLENGES FOR THE FUTURE

A number of important tasks remain. It will be useful to continue to search for new molecular species in diffuse clouds, in order to carry on the testing and refinement of the molecular formation schemes. For example, diatomic species containing silicon may be sufficiently abundant for detection (Turner and Dalgarno 1977), as may some larger molecules such as H_2O (already tenatively identified), C_3 NH_3, CH_2, and CH_3 (Black and Dalgarno 1977). In many of these cases, the laboratory data are incomplete, so that the wavelength at which to search, or the *f* - value, or both are not known. Further work on N_2 and HCl seems justified, since both are expected to appear at levels above or near the current upper limits. For these species, whose best transitions are in the ultraviolet, new instrumentation will be required, since present UV instruments are either too insensitive at the required wavelengths (as in the case of *Copernicus*), or have insufficient resolution and photometric accuracy (IUE).

A new class of molecules has been proposed to exist in diffuse clouds. These are carbon chains, which have been detected in the radio spectrum of dark clouds (Broten et al. 1978; Gardner, Whiteoak, and Winnewisser 1978), and which have been proposed as possible carriers of the diffuse interstellar bands (Douglas 1977; Thaddeus 1978). The optical spectra of such species must be determined before a sensible search can be performed, although at least one progenitor to such species, C_3, can be sought now. Very recent work by Clegg, Lambert and Snell (1979) has failed to detect C_3 absorption in the spectra of ζ Oph and the heavily-reddened supergiant HD143183, but the f-value of the 0-0 band at 4050Å is not known, so the significance of this result is unclear.

Regardless of the validity of the carbon-chain hypothesis, the diffuse bands pose an interesting challenge which may well fall into the province of the molecular spectroscopist. Smith, Snow, and York (1977) reviewed the properties of these bands, which appear in the spectra of all reddened stars, and suggest that a molecular origin is more satisfactory in many ways than the chief alternative, absorption resonances in solid grains. The challenge for the observer is to obtain high-resolution profiles of diffuse bands with the highest possible photometric accuracy to search for possible fine structure; the challenge for the spectroscopist is to seek species, preferably composed of cosmically abundant elements, which reproduce these profiles and wavelengths.

Optical observations of interstellar molecules can be a frustrating endeavor, because of the paucity of laboratory data and the difficulties inherent in detecting very weak absorption lines. On the other hand, it can be a very rewarding area in which to work, because of the close interaction between observation and theory, and because significant observations often are concise and readily-defined. It is exciting to contemplate the new developments which are sure to occur in years to come, particularly with the advent of increasingly sophisticated observational techniques.

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DISCUSSION FOLLOWING SNOW

Mouschovias: Do you have a favorite number for the cosmic-ray ionization rate and, if so, does this rate correlate with the gas density?

Snow: I do not. Furthermore, molecular data are not available for a sufficiently large number of diffuse clouds to estimate cosmic ray ionization rates or densities, so I don't think an adequate data base exists to permit such a correlation to be sought.

Bok: You have a range of kinetic temperatures for your coolest clouds of 50 K to 75 K. Have you any evidence for clouds with temperatures of 10 K to 20 K - as shown by radio CO observations?

Snow: We have one C_2 result (Snow 1978) that implies a value $T_{kin} \lesssim 16$ K for the ζ Ophiuchi cloud. There are uncertainties in this result, due to low data quality and to apparent inconsistencies in the oscillator strengths. For the same cloud, de Boer and Morton (referred to in Morton 1975) derived a value $T_{kin} = 19$ K for observations of fine-structure excitation in atomic carbon. It is possible that diffuse clouds contain very cold core regions, and that the values of T_{kin} derived from the H_2 results refer to a larger volume containing warmer gas.

Kirby: It's not surprising that NaH has not been observed, as calculations by Kirby and Dalgarno (1978) show that, if it were formed on grains, it would be photo-dissociated very rapidly in the interstellar radiation field. Considering the abundance of Mg relative to Na, it would seem that MgH might be a more likely candidate for a search.

Snow: The search for NaH was based on a hypothesis that it might be formed with great efficiency on grains, then ejected and quickly dissociated, accounting for the low depletion of sodium from the gas. Therefore, we thought it a reasonable candidate for a search because of its suggested high formation rate, despite knowing that it probably also has a high destruction rate. While it's true that Mg is more abundant than Na, it is also true that Mg is highly depleted from the gas and is largely bound up in solid grains. I know of no suggestions that MgH is formed rapidly.

Winnewisser: What do you think are the reasons for the low column densities of molecules such as NaH, MgH, etc. Are they frozen out during formation?

Snow: My guess is that these species are not readily formed in diffuse clouds, although we have hypothesized that NaH would be relatively easily formed on grains, *if* this mechanism is important at all. It may not be. In any event, a more likely destruction mechanism is photo-dissociation, since we are talking about diffuse clouds rather than dark clouds.

Thaddeus: There is no example to my knowledge of optical absorption spectroscopy through a bona fide molecular cloud. What in your opinion is the prospect with new photo-detectors of finding a nova or other bright distant object, with more than, say, 10 magnitudes of extinction?

Snow: Certainly modern detection techniques will enhance our

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ability to take advantage of such an opportunity, should one arise. I don't know of anyone who has made specific plans to do this, but I think a number of observers would react quickly. I certainly agree that optical measurements of molecular species should have high priority whenever we get a chance to make absorption-line observations of a dense molecular cloud.

Radhakrishnan: Is there any evidence from UV observations of a correlation between temperature and the peculiar velocity of clouds?

Snow: I know of none. It would be very difficult to look for, because peculiar-velocity clouds are usually low column density, secondary components, in lines of sight that are probed optically. Therefore the kinetic temperatures that are derived refer to the dominant, low-velocity clouds, rather than any high-velocity clouds that may be present.