

ULTRAVIOLET, VISIBLE, AND INFRARED SPECTROSCOPY OF INTERSTELLAR MOLECULES

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ABSTRACT. Absorption line spectroscopy in the ultraviolet, visible, and infrared regions can provide important probes of interstellar chemistry. Significant recent developments include the application of optical absorption line techniques to the study of thick molecular clouds and the improvements in infrared detectors that will eventually lead to effective interstellar spectroscopy in the infrared. Demands for basic molecular data will grow in scope and in level of precision.

1. INTRODUCTION

Owing to improvements in detectors and in astronomical spectrographs, optical observations can now be applied to very thick interstellar clouds and to the investigation of finer details of the internal structure of diffuse clouds. As a result, the demand for basic spectroscopic data on simple molecules is expanding in scope and is becoming more severe with respect to precision. In some cases, exploratory work is needed to identify the electronic and vibrational spectra of important interstellar molecules like C_3H and C_3H_2 . In other instances, there are continuing needs for accurate oscillator strengths and for the resolution of discrepancies between experimental and theoretical determinations of them. Even in cases of well studied molecular spectra like those of CH and CN , the measurement of line positions needs to be improved in accuracy by an order of magnitude or more to satisfy existing needs in the interpretation of astronomical observations.

The number of interstellar molecules detected by optical methods has not increased much since earlier reviews of the subject were completed (Snow 1980; Black 1985; Federman 1987). In the meantime, however, upper limits have been obtained for additional species and the variety of interstellar clouds investigated through known molecules has grown. A recent list of molecules sought by optical methods in diffuse clouds can be found in van Dishoeck and Black (1988a). In particular, no polyatomic molecule has been detected in the interstellar gas by optical absorption measurements. The impending launch of the *Hubble Space Telescope (HST)* promises more sensitive, new searches for molecules in the ultraviolet. Improvements in infrared spectroscopy should open up a new realm of molecular studies in the next few years. In this brief review, recent astronomical results that illustrate needs for molecular data are considered. Some recent developments in molecular studies relevant to astrochemistry are summarized. Finally, an attempt is made to anticipate some paths that the subject might profitably follow in the future.

2. BASIC SPECTROSCOPY

Many of the molecules of astrochemical interest are radicals and ions that lack detailed spectroscopic analyses. Moreover, there exist some stable, unreactive species for which no high-resolution spectroscopy has been performed in the ultraviolet. Although most of the previously unidentified interstellar absorption lines in the ultraviolet spectrum of ζ Ophiuchi have since been assigned to H_2 , HD, and atomic carbon, there remain as many as 19 unidentified interstellar lines at $\lambda = 1023 - 1317 \text{ \AA}$, some of which might be molecular (Morton 1978). We can expect that the number of unidentified ultraviolet lines will increase when the *Hubble Space Telescope* finally reaches orbit.

Interstellar absorption lines of CH were first identified more than 50 years ago (Swings and Rosenfeld 1937), yet increasing demands on the spectroscopy of CH continue to the present day. The widely observed interstellar CH feature $\text{A}^2\Delta - \text{X}^2\Pi$ (0,0) $R_f(1/2)$ is a closely spaced Λ -doublet (wavelengths 4300.3030 and 4300.3235 \AA in standard air) which has never been resolved in astronomical spectra. With the recognition that some diffuse interstellar clouds exhibit complex Doppler velocity structure in multiple components on scales of 0.3–1.0 km s^{-1} (corresponding to wavelength shifts of 0.004–0.014 \AA at 4300 \AA), the accurate description of the intrinsic line shape (i.e. doublet structure in this example) becomes essential to the interpretation of the observations (Black and van Dishoeck 1988a). Laboratory measurements adequate for this purpose have only recently become available (Brazier and Brown 1984; Bernath 1987). Furthermore, the mean wavelength of the 4300 \AA line blend differs by 0.008 \AA (i.e. 0.54 km s^{-1} in Doppler velocity) from the value previously adopted in the astronomical literature. The wavelengths of the interstellar lines of the $\text{B}^2\Sigma^- - \text{X}^2\Pi$ (0,0) band of CH have also been determined much more accurately (P. F. Bernath, preliminary results, as quoted by Black and van Dishoeck 1988a).

Interstellar absorption lines of CN are used not only to study its abundance and chemistry, but also as an indirect radiometric sensor of the cosmic background radiation, which governs the rotational excitation of CN in interstellar clouds of low density. In denser regions, the measurement of excess excitation can be used to estimate the electron density. The most recent observations of CN in diffuse clouds (Meyer and Jura 1985; Crane *et al.* 1986) determine the relative populations in the $N = 0$ and $N = 1$ rotational levels (or the excitation temperature) to approximately $\pm 1\%$ accuracy. At this level, the extraction of the true values of the column densities and the excitation temperature from the measurements can be quite sensitive to very small amounts of line saturation. The unresolved spin-doublets of the $\text{CN B}^2\Sigma^+ - \text{X}^2\Sigma^+$ (violet) system have traditionally been treated as single, unresolvable lines. In fact, the B-X (0,0) $R(0)$ feature is a blend of $R_1(0)$ and $RQ_{21}(0)$ lines with respective relative strengths of 2/3 and 1/3 and with a separation estimated to be 0.0035 \AA (0.27 km s^{-1} in Doppler velocity) on the basis of published spectroscopic constants (Engleman 1974). This small splitting is uncertain and needs to be determined more accurately. There exist observed interstellar CN lines (Meyer and Hawkins 1987) for which the neglect of the unresolved structure would cause a 40% overestimate of the ground-state column density if the Doppler line broadening parameter were as small as $b = 0.5 \text{ km s}^{-1}$ (van Dishoeck and Black 1989).

Spectroscopic studies of small, carbon-bearing molecules of astrophysical interest have produced interesting results recently. The $\text{B}^4\Sigma_u^- - \text{X}^4\Sigma_g^-$ electronic transition of C_2^+ has been identified (O'Keefe *et al.* 1984; Forney *et al.* 1987) and subsequently given a rotational analysis (Rösslein *et al.* 1987). The (0,0) band is calculated to have an oscillator strength $f_{00} = 0.0156$ (Rosmus *et al.* 1986), and potential interstellar absorption lines are at convenient wavelengths: (0,0) $R(1)$, 5065.19 \AA ; $R(3)$, 5063.29 \AA . However, C_2^+ reacts rapidly with H_2 ; therefore, its interstellar abundance is predicted to be quite low. Abundances of

the related ions C_2H^+ and $C_2H_2^+$ are likely to be higher and similar spectroscopic analyses of them would be valuable. Photoelectron spectroscopy of $C_2H_2^+$ indicates that the origin of the $\tilde{A}^2A_g-\tilde{X}^2\Pi_u$ system should lie near $\lambda = 2533 \text{ \AA}$ (Reutt *et al.* 1986). Moreover, the ν_3 fundamental band of this ion has been observed directly at $\tilde{\nu} = 3136 \text{ cm}^{-1}$ (Crofton *et al.* 1987). Further exploratory spectroscopy is also needed for the ion C_2N^+ , whose interstellar abundance may be high (Hartquist and Dalgarno 1980) and whose rotational spectrum has been investigated through theoretical calculations (Kraemer *et al.* 1984; Jensen and Kraemer 1988). The electronic spectrum of the neutral CCN is fairly well known (see Brazier *et al.* 1987 and references therein). It would also be of great interest to know about the electronic transitions of the first interstellar ring molecule, cyclopropenylidene (C_3H_2), because it is observed to be widespread and abundant even in diffuse clouds (Cox *et al.* 1988) through its pure rotational transitions. Electronic and vibrational spectra of C_3H , which has been observed in both cyclic and linear forms, would be of interest.

The C_3 molecule is observed in comets and carbon stars and has been sought unsuccessfully in interstellar clouds through its $\tilde{A}^1\Pi_u-\tilde{X}^1\Sigma_g^+$ transition at 4050 \AA (Clegg and Lambert 1982; Snow *et al.* 1988). C_3 is expected to have an ultraviolet transition $^1\Sigma_u^+-\tilde{X}^1\Sigma_g^+$ with a very large oscillator strength, $f \approx 0.9$ (Römel't *et al.* 1978). Although ultraviolet absorption at 1580 \AA has been attributed to C_3 (Shinn 1982) and matrix isolation studies indicate that the $(0,0,0)-(0,0,0)$ band occurs near 1893 \AA (Chang and Graham 1982), a rotational analysis based on a gas-phase spectrum is still needed. More recently, the ν_3 fundamental vibration-rotation band of C_3 has been identified and analyzed in the spectrum of the carbon star IRC+10216 (Hinkle *et al.* 1988) and in laboratory spectra (Matsumura *et al.* 1988). The oscillator strength of this band is large for an infrared transition (Kraemer *et al.* 1984), and interstellar C_3 is potentially observable in thick clouds through absorption lines near $4.9 \text{ }\mu\text{m}$ wavelength. Positions of the interstellar absorption lines of the Phillips system of C_2 can now be determined much more precisely as a result of the work of Douay *et al.* (1988). The C_2H molecule, which is widely observed through its rotational transitions at millimeter wavelengths, has an electronic transition in the infrared (Curl *et al.* 1985) for which transition moments have been calculated (Reimers *et al.* 1985).

As high-resolution infrared spectrometers with more sensitive array detectors come into operation, infrared spectroscopy of interstellar molecules will begin to play a significant role in astrochemistry. The most abundant interstellar molecule, H_2 , has been essentially unobservable in thick, quiescent molecular clouds, although it can be observed by means of ultraviolet absorption lines in thin, diffuse clouds and through infrared emission lines from molecular gas that is highly disturbed by shock waves or exposed to intense ultraviolet radiation. The fact that its infrared lines are weak dipole-forbidden, electric quadrupole transitions would seem to preclude absorption line studies; however, column densities of H_2 of the order of 10^{23} cm^{-2} or less are in principle detectable in absorption in the $(1,0) S(0)$ and $S(1)$ vibration-rotation lines toward suitably located infrared sources. In this instance, "detectable" refers to an equivalent width $W_\nu \leq 0.01 \text{ cm}^{-1}$ at $\lambda = 2.1 - 2.2 \text{ }\mu\text{m}$, which requires only a signal/noise ratio of 10 or more at a resolving power $\lambda/\Delta\lambda \approx 10^5$. Moreover, it should be possible to observe infrared absorption lines of CO and H_2 simultaneously and thus to make direct determinations of the CO/ H_2 abundance ratio, which is important for quantitative studies of the distribution of molecular material and the efficiency of star formation in galaxies (Williams 1985; van Dishoeck and Black 1987). The infrared absorption lines of interstellar CO have already been detected, both in actively star-forming regions (Hall *et al.* 1978; Scoville *et al.* 1983; Geballe and Wade 1985) and in a quiescent cloud (Black and Willner 1984). Solid CO that has frozen onto interstellar grains has been identified through its distinctive infrared absorption spectrum (Hagen *et al.* 1980; Lacy *et al.* 1984; Larson *et al.* 1985; Whittet *et al.* 1985; Geballe *et al.* 1985; Geballe 1986). Recent

laboratory investigations have also made it possible to determine the column density of solid CO and to infer something about the surface chemistry (Sandford *et al.* 1988). Laboratory spectroscopy of other astrophysical ices has also been pursued (e.g. d'Hendecourt and Allamandola 1986, and references therein).

Infrared absorption line spectroscopy can provide significant tests of theories of interstellar chemistry, especially with respect to the abundances of important non-polar species like H_3^+ , CH_4 , and C_2H_2 , which are otherwise not readily observable in interstellar space. The infrared absorption lines of H_3^+ at $\lambda = 3.7 - 4.1 \mu\text{m}$ are expected to be detectable both in dark molecular clouds (Oka 1981) and in classical diffuse clouds (van Dishoeck and Black 1986; Black and van Dishoeck 1988b). Knacke *et al.* (1985) have reported a recent search for interstellar CH_4 . Table 1 lists a selection of infrared transitions of actual or potential interstellar molecules that will be important for absorption line studies. The table presents band or line frequencies in cm^{-1} and, where information on oscillator strengths is available, a characteristic column density required to produce an absorption feature of equivalent width $W_\nu = 0.01 \text{ cm}^{-1}$.

Metal atoms and ions may play a major role in the ionization balance of interstellar clouds, but very little is known about their participation in interstellar chemistry. Many metal-containing molecules have strong, well known transitions in the visible region. However, no molecules containing Mg, Ca, Na, Fe, or Ti have been found in the interstellar medium, with the possible exception of a detection of MgO at millimeter wavelengths. No sensitive optical searches for molecules like MgO and TiO have ever been reported in the literature. In view of the possibility that TiO^+ forms by an exothermic chemi-ionization process in interstellar clouds, $\text{Ti} + \text{O} \rightarrow \text{TiO}^+ + e^-$, it would be interesting to know something about the spectrum of this ion (Oppenheimer and Dalgarno 1977, Black 1988).

The subject of very large molecules (e.g. polycyclic aromatic hydrocarbons = PAHs) in interstellar space is very fashionable (see, e.g., Omont 1986, Lepp and Dalgarno 1988, and references therein) and much spectroscopic work remains to be done. Although PAHs have joined the long list of possible carriers of the diffuse interstellar bands (Josafatsson and Snow 1987 and references therein), no specific and convincing identification has been made. The large molecule buckminsterfullerene, C_{60} , has recently been shown to have an isolated, narrow absorption band at 3860 \AA (Heath, Curl, and Smalley 1987).

3. QUANTITATIVE SPECTROSCOPY

Molecular abundances can be determined and quantitative tests of chemical models can be made only if oscillator strengths of molecular transitions are known. Only a few recent developments can be summarized here; for a recent review, see Smith (1987). Although detections or upper limits have been reported for at least 34 molecules in diffuse clouds (see Table 1 of van Dishoeck and Black 1988a), several of the limits are not very useful owing to the lack of information on oscillator strengths. Specifically, oscillator strengths are needed for ultraviolet transitions of MgH^+ , SH, CaH, and SiO. Naturally, oscillator strengths will also be needed for various species whose electronic spectra have not yet been identified and analyzed (see §2 above).

The red systems of $\text{CN } A^2\Pi - X^2\Sigma^+$ and $\text{C}_2 A^1\Pi_u - X^1\Sigma_g^+$ are now being used for absorption line studies of diffuse and translucent clouds (van Dishoeck and Black 1989). Although much effort has been devoted to the determination of the oscillator strengths of these systems, there remain some unresolved questions. Recent experiments are in harmony for the $\text{C}_2 A - X$ Phillips system (Erman *et al.* 1982; Bauer *et al.* 1985, 1986; Davis *et al.* 1984) with $f_{00} \approx 1.4 \times 10^{-3}$ and $f_{20} \approx 1.0 \times 10^{-3}$; however, oscillator strengths determined

Table 1. SELECTED INFRARED TRANSITIONS OF INTERSTELLAR MOLECULES

Species	Transition	$\tilde{\nu}$ (cm ⁻¹)	N_0 (cm ⁻²)
H ₂	$v = 1 - 0$ S(0)	4497.8391	1.2(23)
H ₃ ⁺	$\nu_2 = 1 - 0$ ^R R ₁ (1)	2891.444	1.3(14)
H ₂ D ⁺	$\nu_1 = 1 - 0$ 1 ₀₁ - 0 ₀₀	3038.177	2.3(15)
	$\nu_3 = 1 - 0$	2329.	4.9(14)
HeH ⁺	$v = 1 - 0$ R(0)	2972.91	7.6(13)
H ⁸⁵ Cl	$v = 1 - 0$ R(0)	2908.2474	1.8(15)
CO	$v = 1 - 0$ R(0)	2147.081	1.1(15)
	$v = 2 - 0$ R(0)	4263.83734	1.5(17)
CN	A ² Π-X ² Σ ⁺ (0,0) R ₁ (0)	9094.3192	6.6(12)
	$v = 1 - 0$	2046.13	2.6(15)
	$v = 2 - 0$	4062.26	8.0(15)
CH ⁺	$v = 1 - 0$ R(0)	2766.5341	3.4(16)
CH	$v = 1 - 0$ R ₂ (1/2)	2796.883, 2797.008	6.0(14)
CH ₂	$\nu_1 = 1 - 0$	3020.7	
	$\nu_3 = 1 - 0$	3152.5	
CH ₃	$\nu_3 = 1 - 0$ 1 ₁ - 0 ₀	3174.2935	6.0(15)
CH ₄	$\nu_3 = 1 - 0$	3019.	9.4(14)
HC ₃ N	$\nu_1 = 1 - 0$ R(0)	3327.680	
C ₂	A ¹ Π _u -X ¹ Σ _g ⁺ (0,0) Q(2)	8267.1336	1.6(13)
	A ¹ Π _u -X ¹ Σ _g ⁺ (1,0) Q(2)	9851.1169	1.4(13)
	A ¹ Π _u -X ¹ Σ _g ⁺ (2,0) Q(2)	11410.84115	2.3(13)
C ₃	$\nu_3 = 1 - 0$	2042.665	9.7(13)
C ₂ H	$\tilde{A}^2\Pi(0,0,0)$ - $\tilde{X}^2\Sigma^+(0,0,0)$	3772-4108	1.0(14)
C ₂ H ₂	010(11) ₀ ⁰ R(1)	3286.585	2.4(15)
	0010 ⁰ 0 ⁰ R(1)	3299.521	2.9(15)
	1000 ⁰ 1 ¹ Q(1)	4091.170	6.2(16)
	0100 ⁰ 3 ¹ Q(1)	4138.883	
HCO ⁺	$\nu_1 = 1 - 0$ R(0)	3091.679	
HCN	$\nu_3 = 1 - 0$	3311.	1.0(15)
DCN	$\nu_3 = 1 - 0$	2630.	1.8(15)
C ³² S	$v = 1 - 0$ R(0)	1273.7898	
OH	$v = 1 - 0$ Q ₁ (3/2)	3568.47	9.1(15)
NH ₂	$\nu_1 = 1 - 0$ 1 ₁₁ - 0 ₀₀	3250.54	
	$\nu_3 = 1 - 0$ 1 ₀₁ - 0 ₀₀	3322.50	
SH	$v = 1 - 0$	2598.03	
HF	$v = 1 - 0$ R(0)	4000.9894	6.4(14)

Note: The characteristic column density, N_0 , is that required to produce a feature with an equivalent width of 0.01 cm⁻¹ in the weak-line limit. Each transition is designated either as a band or as an individual line. In the former case, the characteristic column density refers to a sum over all lower rotational levels; in the latter case, the column density is that in the lower level of the line.

from *ab initio* theoretical calculations remain factors of 1.5 - 2 larger (van Dishoeck 1983; Chabalowski et al. 1983; Pouilly et al. 1983; ONeil et al. 1987; Klotz 1987). Theory and

experiment are similarly discrepant for the A–X system of CN (Cartwright and Hay 1982; Larsson *et al.* 1983; Davis *et al.* 1986; Taherian and Slanger 1984; Sneden and Lambert 1982), although very recent calculations (Bauschlicher *et al.* 1988) come closer to experiment. Since the oscillator strength of the B–X system is well established, consistency tests can be carried out by astronomical spectroscopy for a few regions where both the violet and red system lines of interstellar CN are observed.

There remains an unresolved disagreement between two lifetime measurements for the \tilde{A} – \tilde{X} system of H_2O^+ (Möhlmann *et al.* 1978; Curtis and Erman 1977), which is significant in view of the very low limits that have been placed on the strengths of its interstellar absorption lines in several clouds (see Federman 1987). This is important for the study of cometary spectra as well (see Lutz 1987).

In the Lyman and Werner systems in the ultraviolet spectrum of H_2 , non-adiabatic rotational perturbations affect the oscillator strengths of individual rotational lines: the calculated line strengths of Ford (1975) have recently been extended to a larger number of transitions by Abgrall *et al.* (1987). Accurate transition probabilities in the ν_2 vibration-rotation band of H_3^+ have been calculated by Miller and Tennyson (1988).

Another important aspect of quantitative spectroscopy concerns information that is required for the full description of processes like photodissociation. One example of much current interest is the photodissociation of CO, which evidently occurs principally through pre-dissociating lines rather than by continuous absorption in the interstellar medium. Information on line positions, isotopic shifts, oscillator strengths, and pre-dissociation widths is becoming available as a result of diligent efforts by Eidelsberg *et al.* (1984), Letzelter *et al.* (1987), Stark *et al.* (1987), and Yoshino *et al.* (1988). The new spectroscopic data have already been applied to theoretical models of the CO chemistry in circumstellar envelopes (Mamon *et al.* 1988) and in interstellar clouds (Viala *et al.* 1988; van Dishoeck and Black 1988b). The rate of photodissociation of CO depends upon the intensity of ultraviolet starlight and on the oscillator strengths of the dissociating lines, while the depth-dependence of the absorption is governed partly by the line broadening which has a significant contribution from the pre-dissociation itself. Observationally, the translucent clouds may provide the most important tests of our understanding of the CO photochemistry in that they occupy the realm of parameter space in which CO is just beginning to account for a large fraction of the gas-phase carbon and oxygen. Ultraviolet absorption line observations with the High Resolution Spectrograph on *HST* promise to be of some value in this regard since there are many strong bands of the $\text{A}^1\Pi\text{--X}^1\Sigma^+$ 4th-positive system at wavelengths as long as 1544 Å. On the other hand, these absorption features will be strongly saturated in translucent clouds, and the interpretation will be quite complicated owing to the dense rotational structure of these bands, which will at best be barely resolved at the highest resolution of the High Resolution Spectrograph. The fundamental and first overtone vibration-rotation bands of CO at 4.6 and 2.3 μm will eventually provide an important alternative source of information on the abundance and excitation of this molecule. Although atomic spectroscopy is outside the purview of this review, the chemistry of simple carbon-bearing molecules cannot be fully understood without knowledge of the abundances of C and C^+ . *HST* is expected to make possible sensitive interstellar absorption measurements of the C II] intersystem multiplet near 2325 Å; therefore, it is important to determine the small oscillator strengths of these lines as accurately as possible (Nussbaumer *et al.* 1981; Stencel *et al.* 1981; Hobbs *et al.* 1982; Cowan *et al.* 1982; Lennon *et al.* 1985).

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