2. FORMATION OF MOLECULES

https://doi.org/10.1017/S153929960000037X Published online by Cambridge University Press

LABORATORY STUDIES OF THE SPECTRA OF INTERSTELLAR MOLECULES

G. HERZBERG
Division of Physics,
National Research Council of Canada, Ottawa, Canada

1. Introduction

During the last twenty years many studies have been carried out in our laboratory which were aimed at establishing the exact positions of possible sharp interstellar lines of various diatomic and polyatomic molecules. In addition we have been trying to see whether the diffuse interstellar lines cannot be explained as produced by some molecule or molecular ion in the interstellar gas.

The present report is a summary of our recent work in this field.

2. Sharp Line Spectra

Of the many studies in the optical region I shall mention only a very few. A great deal of effort has been spent on the spectra of molecular hydrogen [1]. Table I gives the $R(0)$, $R(1)$ and $P(1)$ lines of some of the Lyman bands as derived from these studies as well as the $R(0)$, $R(1)$ and $Q(1)$ lines of some of the Werner bands [2]. The Werner bands are of about the same intensity as the Lyman bands and must be

TABLE I

Expected interstellar absorption lines of H_2
(Lyman and Werner bands)

	v'–v''	$R(0)$	$R(1)$	$P(1)$, $Q(1)$
B–X	0–0	1108.13	1108.64	1110.06
	1–0	1092.20	1092.73	1094.05
	2–0	1077.14	1077.70	1078.93
	3–0	1062.88	1063.46	1064.61
	4–0	1049.37	1049.96	1051.03
	5–0	1036.55	1037.15	1038.16
	6–0	1024.37	1024.99	1025.94
	7–0	1012.81	1013.44	1014.33
	8–0	1001.82	1002.45	1003.30
	9–0	991.38	992.02	992.81
	10–0	981.44	982.07	982.84
	11–0	971.99	972.63	973.35
C–X	0–0	1008.56	1008.53	1009.77
	1–0	985.64	985.66	986.79
	2–0	964.99	965.07	966.09

De Jager (ed.), Highlights of Astronomy, 415–420.

considered in the interpretation of interstellar absorption spectra. If the molecular hydrogen were in thermal equilibrium only $R(0)$ lines corresponding to para-H_2 would appear. It seems likely, however, that such an equilibrium does not exist (as suggested by the observations on formaldehyde) and in that case the $R(1)$, $P(1)$ and $Q(1)$ lines (ortho-H_2) would also be observable.

In Table II corresponding data for D_2 partly based on unpublished work in this laboratory are presented.

TABLE II

Expected interstellar absorption lines of D_2 (Lyman and Werner bands)

	$v'-v''$	$R(0)$	$R(1)$	$P(1)$, $Q(1)$
$B-X$	0–0	1103.1	1103.4	1104.1
	1–0	1091.8	1092.1	1092.7
	2–0	1080.9	1081.2	1081.8
	3–0	1070.4	1070.7	1071.3
	4–0	1060.4	1060.7	1061.3
	5–0	1050.7	1051.0	1051.5
	6–0	1041.4	1041.7	1042.2
	7–0	1032.4	1032.7	1033.2
	8–0	1023.7	1024.0	1024.5
	9–0	1015.4	1015.7	1016.1
	10–0	1007.3	1007.6	1008.1
	11–0	999.5	999.8	1000.3
	12–0	992.0	992.3	992.7
	13–0	984.8	985.1	985.5
$C-X$	0–0	1005.8	1005.8	1006.4
	1–0	989.3	989.3	989.9
	2–0	974.0	974.0	974.5

Douglas and Lutz [3] have recently observed the spectrum of SiH^+ in emission in a discharge tube. In view of the presence of CH^+ in the interstellar medium it seems possible that SiH^+ may also be present. The expected interstellar lines are given in Table III.

TABLE III

Predicted interstellar absorption lines of OH and SiH^+. (Douglas [4] and Douglas and Lutz [3])

Molecule	Transition	Line	λ
OH	$D^2\Sigma^- - X^2\Pi$ 0–0	$R_1(\frac{3}{2})$	1221.166 Å
		$Q_1(\frac{3}{2})$	1222.071 Å
		$P_1(\frac{3}{2})$	1222.520 Å
SiH^+	$A^1\Pi - X^1\Sigma^+$ 0–0	$R(0)$	3993.400 Å
	1–0	$R(0)$	3932.347 Å

Quite recently Douglas [4] observed a new absorption band of OH near 1220 Å. This absorption band is substantially stronger than the well-known band at 3060 Å. The predicted interstellar lines are included in Table III.

No infrared spectra of interstellar molecules have as yet been found but with the improvement of infrared techniques particularly of the Fourier method developed to such high perfection by Connes, it should be possible to detect the infrared bands not only of those molecules that have been established by radio astronomers, like NH_3, H_2O, H_2CO and HCN, but also those molecules like C_2H_2 and CH_4 which because of the absence of a permanent dipole moment cannot be detected by radio-frequency methods.

I suggested three years ago at the meeting on laboratory astrophysics at Lunteren, Holland, that interstellar CH_4 may be seen in Connes' spectrum of α Orionis even though the observed peaks are hardly greater than the noise in the spectrum. Since that time NH_3, H_2O, H_2CO and HCN have been discovered to be present and it seems now almost a foregone conclusion that CH_4 is also present. At any rate the rather doubtful evidence for CH_4 in Connes' spectra gives at least an upper limit to the amount of CH_4 present, namely, 1.3×10^{-5} molecules/cm^3. It must be emphasized that this estimate is based on the assumption that there is low temperature equilibrium in CH_4. Actually the presence of two other modifications of CH_4 (similar to ortho and para-H_2) would make the upper limit still higher. It might also be mentioned that in order to ascertain which are the most likely lines to be observed in interstellar absorption new absorption spectra of CH_4 in the laboratory have been taken. In this way the $R(0)$ lines have been identified in the bands at 4546 and 4313 cm^{-1} which had not previously been analysed.

Dr Connes is planning to take, with improved equipment, new spectra of α Orionis at times when the shift between interstellar and terrestrial lines is expected to be different from that in the old spectra. If this is found to be the case, it will be possible to establish whether CH_4 is indeed present in the interstellar medium.

3. Diffuse Spectra

Many of the now known interstellar molecules show diffuse lines in their ultraviolet absorption bands. This diffuseness is caused by the phenomenon of predissociation, that is, the possibility that the molecule in the excited state, instead of returning to the ground state, will go over by a radiationless transition into a continuous range of energy levels of equal energy corresponding to dissociation. This phenomenon was first established by laboratory investigations of NH_3 [5]. Other examples have been found in HCN [6], H_2O [7] and HCO [8]. Even for the diatomic CH molecule at 1560 Å an absorption band with distinctly diffuse lines has been observed [9] and it has been shown that the strong absorption at 3140 Å is very slightly diffuse. It is significant that even though almost every absorption of a photon in the diffuse absorption bands leads to dissociation of the absorbing molecule, that is, even though the destruction rate is high, these molecules (CH, NH_3 etc.) are known to be present.

There are many other molecules for which diffuse absorption lines have been found in the laboratory. Some of these are almost certainly present in the interstellar medium like HCO [8], CH_3 [10], CH_2 [10], and possibly SiH [11].

In view of the known presence of molecules which show diffuse absorption lines in the ultraviolet it seems natural to suggest that the observed diffuse interstellar lines in the visible region are also produced by some not yet identified interstellar molecule or molecules, that is, that their diffuseness results from a predissociation process. A radical that does have diffuse absorption lines in the visible region is HCO but the wavelengths of these lines do not agree with those of the diffuse interstellar lines.

For the reasons given I have tried for several years to look for other molecules with diffuse absorption lines in the visible region in the hope of finding one that would give agreement with the diffuse interstellar lines. The molecule to be found must be a relatively abundant molecule and it must have a sufficiently small dissociation energy so that predissociation can arise at a wavelength of 6284 Å (the wavelength of the most longward diffuse interstellar line).

In view of the high relative abundance of hydrogen it seems likely that the molecule we are looking for contains mostly hydrogen and at most one other, less abundant atom. A system containing only hydrogen would be H_3^+ but calculations in the last few years [12] have shown that its dissociation energy is fairly large, too large to be considered for the present purpose. Other molecules that we have considered are NH_4, H_3O, CH_5 and CH_4^+. All of these are known to have low dissociation energies and are expected to show absorption in the visible region.

Experiments were therefore carried out to try and obtain absorption spectra of these systems. NH_4, H_3O and CH_5 were looked for by means of the flash photolysis of mixtures of NH_3, H_2O and CH_4 with NH_3 at low temperatures. Since it is known that NH_3 decomposes into NH_2+H it was hoped that the H atoms thus formed would associate with NH_3, H_2O or CH_4 to form NH_4, H_3O or CH_5 respectively. But none of these experiments showed any new spectra which could be identified with the diffuse interstellar lines. The spectrum of CH_4^+ was looked for in absorption in flash discharges and at present experiments are proceeding where, instead, CH_4 is irradiated by a pulsed electron beam in the hope of producing for a very short time a sufficient concentration of CH_4^+. This work also has not yet been successful. However, new photoelectron work by Price, Turner and their associates and still more recently Lindholm and Åsbrink show two peaks in the first group of photoelectrons showing that there are two low-lying states. These two states arise from the expected $^2F_2$ ground state of CH_4^+ by (static) Jahn-Teller interaction. The vibrational structure of the transition between these two states would be sufficiently complicated to account for the rather complicated vibrational structure of the observed interstellar spectrum. Of course, only after a quantitative agreement of the level scheme of CH_4^+ derived from the photoelectron spectrum, or of a laboratory absorption spectrum, with the diffuse interstellar lines has been obtained could one be certain that CH_4^+ is the carrier.

4. Continuous Spectra

In absorption, continuous spectra of molecules are not useful for identification purposes. For example, CH_4 has a continuous absorption starting at about 1400 Å; if one finds an extinction below this wavelength it could however be caused by many other molecules or radicals.

Continuous *emission* spectra are perhaps of greater interest from an astronomical point of view. I should like to discuss one which is produced by the hydrogen molecule (in addition to the well-known continuum which extends from the visible to the ultraviolet region). Stecher and Williams [13] were the first to suggest that molecular hydrogen in the interstellar medium is dissociated by absorption in the discrete region of the Lyman bands followed by continuous emission corresponding to the transition from the upper discrete states to the continuum belonging to the ground state. Dalgarno and Stephens [14] have calculated the intensity distribution in this postulated continuum. There are a number of very pronounced maxima and minima in it. This theoretical intensity distribution agrees exactly with that in a continuum observed several years ago in electric discharges in hydrogen. The fluctuations in this continuum correspond to the maxima of the continuum wave-functions as predicted in 1928 by Condon. This continuum must occur in interstellar emission but it would be difficult to observe since it is necessarily coupled with the strong discrete Lyman bands.

5. Conclusion

The interpretation of the diffuse interstellar lines as predissociated lines of a molecule has been questioned by Wilson [15] who argues that it would lead to too short a life time of this molecule. It appears to me that this argument cannot be maintained since the same argument would lead one to the conclusion that many of the molecules actually observed to be present in the interstellar medium cannot be there since they also have diffuse absorption lines. We simply do not yet know enough about molecule formation in the interstellar medium. At any rate radicals like CH and OH and molecular ions like CH^+ and CH_4^+ could be formed by the photodecomposition of much more abundant parent compounds like CH_4 and H_2O.

References

[1] Herzberg, G. and Howe, L. L.: 1959, *Can. J. Phys.* **37**, 636; Wilkinson, P. G.: 1968, *Can. J. Phys.* **46**, 1225; Herzberg, G.: 1969, *Phys. Rev. Letters* **23**, 1081; Herzberg, G.: 1970, *J. Mol. Spectr.* **33**, 147.

[2] Monfils, A.: 1965, *J. Mol. Spectr.* **15**, 265, 1968, **25**, 513.

[3] Douglas, A. E. and Lutz, B. L.: 1970, *Can. J. Phys.* **48**, 247.

[4] Douglas, A. E.: to be published.

[5] Bonhoeffer, K. F. and Farkas, L.: 1927, *Z. Phys. Chem. A* **134**, 337.

[6] Herzberg, G. and Innes, K. K.: 1957, *Can. J. Phys.* **35**, 842.

[7] Johns, J. W. C.: 1963, *Can. J. Phys.* **41**, 209.

[8] Herzberg, G. and Ramsay, D. A.: 1955, *Proc. Roy. Soc.* **233A**, 34; Johns, J. W. C., Priddle, S. H., and Ramsay, D. A.: 1963, *Discussions Faraday Soc.* **35**, 90.

[9] Herzberg, G. and Johns, J. W. C.: 1969, *Astrophys. J.* **158**, 399.
[10] Herzberg, G.: 1961, *Proc. Roy. Soc.* **262A**, 291.
[11] Herzberg, G., Lagerqvist, A., and McKenzie, B. J.: 1969, *Can. J. Phys.* **47**, 1889.
[12] Conroy, H.: 1964, *J. Chem. Phys.* **41**, 1341; 1969, **51**, 3979; Christoffersen, R. E. 1964: *J. Chem. Phys.* **41**, 960; Christoffersen, R. E. and Shull, H.: 1968, *J. Chem. Phys.* **48**, 1790; Schwartz, M. E. and Schaad, L. J.: 1967, *J. Chem. Phys.* **47**, 5325.
[13] Stecher, T. P. and Williams, D. A.: 1967, *Astrophys. J. Letters* **149**, 29.
[14] Dalgarno, A., Herzberg, G., and Stephens, T. L.: 1970, *Astrophys. J. Letters* **162**, 49.
[15] Wilson, R.: 1964, *Publ. Roy. Obs. Edinburgh* **4**, 67.