RECENT LABORATORY WORK ON MOLECULES OF POSSIBLE IMPORTANCE FOR INTERSTELLAR STUDIES

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One of the aims of our work at the National Research Council (Ottawa) during the last thirty years has been to contribute laboratory data that are of possible astronomical interest especially for the study of the interstellar medium.

NEUTRAL MOLECULES

The detection of the first two interstellar molecules, CH and CN in the near ultraviolet region, needed no special laboratory work since all the information for this identification had been assembled a long time before. As is well known, the radio-frequency detection of CH presented considerable difficulty. Various attempts to determine the Λ-type doubling in the CH ground state, X $^2\Pi$, from the optical spectrum were required (Douglas and Elliott (1965), Goss (1966), Baird and Bredohl (1971)) before this transition was observed by Rydbeck et al. (1974). Even now the radio lines of CH have not been observed in the laboratory.

A considerable amount of work has been done at NRC on the spectra of H_2, HD and D_2. The earlier work on these molecules, with the exception of that of Wilkinson (1968), was marred by the lack of good standards. This was not a difficulty for the new laboratory measurements of HD (Dabrowski and Herzberg (1976)) and as a result the agreement between the Copernicus observations and the laboratory spectra is now excellent.

For the detection of diatomic carbon, that is, the C_2 molecule, it was first necessary to establish the nature of the ground state of this molecule. This was done in the laboratory work of Ballik and Ramsay (1963) who established that the ground state is $^1\Sigma_g^+$. In Figure 1 the known
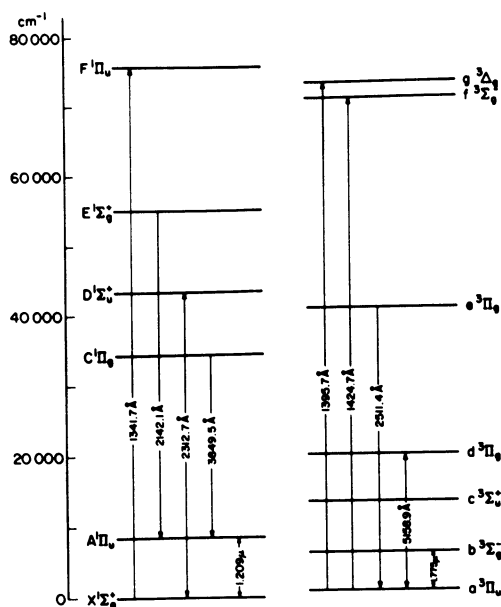
Fig.1. Electronic energy levels and observed transitions in C_2

electronic states of C_2 are presented. It was only last year that the transition from the ground state to the lowest excited state (the Phillips bands) was observed in inter-stellar absorption by Chaffee and Lutz (1978). At the same time Snow (1978) observed in the ultraviolet the Mulliken bands in absorption.

It is surprising that the OH molecule, which was the first molecule identified by radio-astronomy in interstellar space, was only quite recently observed optically, first in the vacuum ultraviolet by Snow (1976) using the 1222 Å band found in the laboratory somewhat earlier by Douglas (1974) and still more recently in the ordinary ultraviolet near 3080 Å by Crutcher and Watson (1976).

In the 1950's the optical spectra of HCO and HNO were discovered at NRC (Herzberg and Ramsay 1955, Dalby 1958). Subsequently microwave spectra were observed in the laboratory by Saito (1972) and Saito and Takagi (1973) and on that basis these two radicals were detected in the interstellar medium by Snyder et al. (1976) and Ulich et al. (1977). It is somewhat surprising to find HCO present in spite of the fact that its dissociation energy is rather small, of the order of 1 eV. It is of interest to mention that HCO in the visible region (near 5400, 5900 and 6460 Å) has diffuse absorption bands (in addition to sharp ones).

The R(0) lines of these bands should be observable in the interstellar medium if sufficient concentrations of HCO are present. However they do not agree with the known diffuse interstellar absorption features.

The spectrum of the NH_2 radical in the optical region was discovered in 1952 (Herzberg and Ramsay) and was analysed by Dressler and Ramsay in 1959. The laboratory work on this spectrum is continuing (Johns, Ramsay and Ross 1976). While some microwave lines have been found in the laboratory by microwave optical double resonance and laser magnetic resonance no features have yet been identified in the interstellar medium. The optical spectrum of NH_2 is, however, a prominent feature in the spectra of the heads of comets.

The CH_2 radical has been found by laboratory experiments to have a triplet ground state ($^3B_1$) and a number of low-lying singlet states (Herzberg 1961, Herzberg and Johns 1971). The optical absorption spectrum lies in the vacuum ultraviolet near 1415 Å. In CH_2, unlike CD_2, the individual rotational lines of the absorption band are fairly diffuse. The R(0) and P(1) lines lie at 1415.50 and 1416.05 Å. It is perhaps significant that Snow, York and Resnick (1977) report in a number of stars as the only diffuse feature in the vacuum ultraviolet one somewhat questionable line at 1416 Å.

The CH_3 radical (Herzberg 1961) has diffuse absorption bands with peaks at 2157.6, 2163.6, 1502.4 and 1496.89 Å. It seems likely that they will eventually be found in interstellar absorption.

Recently we have found (Herzberg 1979) in hollow cathode discharges in hydrogen a number of emission bands which have been definitely assigned as belonging to the Rydberg spectrum of triatomic hydrogen (H_3 and D_3). All rotational lines are diffuse, for H_3 much more so than for D_3. The observed intensity alternation confirms the D_{3h} symmetry of this molecule, i.e. that the nuclei form an equilateral triangle with a H-H distance of 0.87 Å as in H_3^+. The new spectra are emitted in the process of dissociative recombination of H_3^+ and D_3^+. This process has been assumed to be the cause of the eventual destruction of H_3^+ in the interstellar medium. It seems possible therefore that the H_3 spectrum will be observable in astronomical spectra.

MOLECULAR IONS

Recently Alberti and Douglas (1975) have made new measurements of the NO^+ spectrum, first discovered by Baer and Miescher (1953), with the principal aim of having accurate predictions for possible identification of interstellar lines of this ion. Table I summarizes their

Table I. NO^+ lines of astronomical interest

Transition	R(0)
$^1\Pi(v=0)-^1\Sigma(v=0)$	1368.2404
$^1\Pi(v=1)-^1\Sigma(v=0)$	1339.6361
$^1\Pi(v=2)-^1\Sigma(v=0)$	1312.9400
$^1\Pi(v=3)-^1\Sigma(v=0)$	1288.0254
$^1\Pi(v=4)-^1\Sigma(v=0)$	1264.7900
$^1\Sigma(v=1)-^1\Sigma(v=0)$	2347.74 (cm^{-1})
$^1\Sigma(J=1-J=0)$	119187±30 MHz

results. Colbourn and Douglas (1977) made new measurements of N_2^+ and O_2^+ with the same aim. It would seem worthwhile to make an all-out attempt to observe the N_2^+ spectrum since the N_2^+ lines have a high f value and are very conveniently located in the spectrum (3914 Å).

Ms. Dabrowski and I (1977) have used the theoretical potential function of HeH^+ derived by Wolniewicz (1965) and Kolos and Peek (1976) in order to predict the infrared spectrum of this ion. We have also calculated the quasibound levels of this ion which lie above the dissociation limit at 1.845 eV. The inverse predissociation via these quasibound levels may lead to a recombination spectrum that has also been predicted. Attempts in this laboratory to observe the infrared spectrum of HeH^+ have so far been unsuccessful.

Discharges through He-Ne mixtures yield two features near 4200 Å and similar spectra occur near 1400 Å in Ar-He mixtures. Tanaka, Yoshino and Freeman (1975) first correctly recognized the nature of the transitions responsible for these spectra. They are charge transfer spectra in which the molecule goes from a state that is essentially He^+ + Ne to a lower state that is essentially He + Ne^+ and similarly for $HeAr^+$. Figure 2 gives a potential energy diagram for $HeNe^+$ based on a fairly complete analysis of the spectrum near 4200 Å (Dabrowski and Herzberg 1978). The ground state of $HeNe^+$ has a fairly large dissociation energy (0.6 eV). On account of the
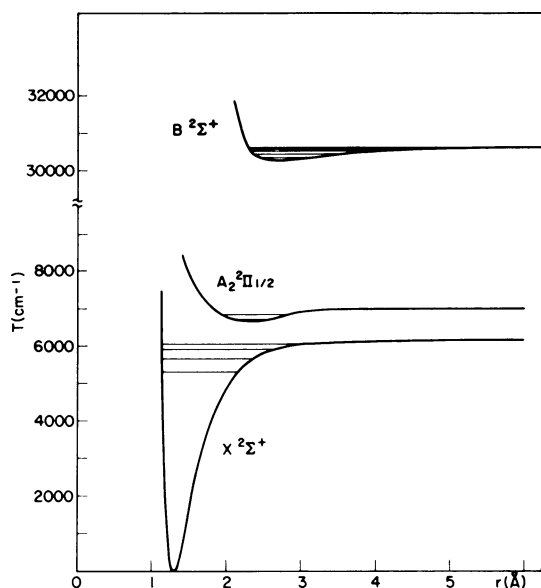
Fig.2. Potential energy functions of HeNe$^+$

Franck-Condon principle we were unable to observe the lowest vibrational levels of the ground state but were able to establish the vibrational numbering on the basis of isotope shifts in ^{3}HeNe$^+$. In the interstellar medium it seems likely that HeNe$^+$ if once formed will reach by infra-red transition the lowest level of the ground state. A microwave line at 173550 MHz and an infrared line at 1280 cm^{-1} are predicted.

As is well known, the ions HCO$^+$ and N$_2$H$^+$ were first observed by radio-astronomical methods before they were observed in the laboratory by Woods et al. (1975) and Saykally et al. (1976) in absorption in electric discharges through suitable gas mixtures. We have attempted, so far unsuccessfully, to observe the ultraviolet spectra of these ions. It seems possible that some of the unidentified interstellar lines in the vacuum ultraviolet might be due to the electronic transition of these molecular ions.

An electronic transition of H$_2$O$^+$, very similar to that of NH$_2$, was first observed by H. Lew (1973, 1976) in emission of hot cathode discharges. In the upper state the ion is essentially linear while in the lower state it is strongly bent with an angle of about 110°. The molecular constants of H$_2$O$^+$ may be found in Dr. Lew's paper. In Table II some of the predicted interstellar lines are listed. None have yet been found.

Table II. Predicted interstellar lines of H_2O^+

a) in the microwave region			b) in the visible region	
Rotational transition	Spin component	Frequency (GHz)	Transition	$\lambda_{lab}(\overset{\circ}{A})$
$2_{20}-3_{13}$	F_1	144.44 ± 0.39	$(0,6,0)-(0,0,0)$	6973.720
	F_2	187.19 ± 0.42		6970.152
$4_{14}-3_{21}$	F_1	134.88 ± 0.40	$(0,8,0)-(0,0,0)$	6146.802
	F_2	103.87 ± 0.39		6147.375
$3_{30}-4_{23}$	F_1	218.61 ± 0.48	$(0,10,0)-(0,0,0)$	5478.548
	F_2	266.56 ± 0.50		5481.217
$4_{22}-3_{31}$	F_1	34.27 ± 0.54	$(0,12,0)-(0,0,0)$	4922.382
	F_2	-13.37 ± 0.54		4917.854
$6_{33}-5_{42}$	F_1	278.89 ± 0.72	$(0,14,0)-(0,0,0)$	4469.358
	F_2	234.41 ± 0.72		4468.823
$6_{52}-7_{43}$	F_1	64.07 ± 1.6		
	F_2	105.63 ± 1.6		

From the photoelectron spectrum of NH_3 it is readily seen that there is an excited state of NH_3^+ at 4.77 eV above the X $^2A_2''$ ground state (assuming D_{3h} symmetry). Therefore an emission spectrum near 2300Å may be expected. Since the excited state is in all probability a $^2E'$ state the transition between it and the ground state is electronically forbidden. However, vibronic interaction will make some of the vibrational transitions in the forbidden electronic transition allowed provided that either in the upper or lower state a degenerate vibration is excited. Using electron bombardment excitation of a NH_3 jet we have observed a number of weak but distinct features in the 2400-2200 Å region. One simple band near 2338 Å appears in which apparently alternate lines are missing. If this were true it would prove that the band is a sub-band of a $\perp$ band in a planar molecule with D_{3h} symmetry as expected for NH_3^+.

The ion-molecule reaction

$$H_2^+ + H_2 \rightarrow H_3^+ + H + 1.75 \text{ eV}$$
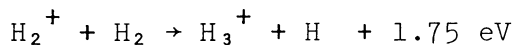
is one of the fastest known reactions. As a result one finds that in every discharge through H_2 the H_3^+ ion is the most abundant ion (except at very low pressure). It is believed that also in the interstellar medium H_3^+ is a fairly abundant ion. It seems to play an important role in the processes that lead to molecule formation (see Herbst and Klemperer 1973, Watson 1973, Suzuki 1979).

In order to detect H_3^+ spectroscopically one is
dependent on its infrared bands since according to
theoretical calculations all excited electronic states
seem to be unstable. Up to now the infrared spectrum has
not been observed in the laboratory. However, H. Lew,
J. Sloan and I at Ottawa have made a number of attempts to
observe this spectrum in emission from a hollow cathode
discharge cooled to liquid nitrogen temperature. Using a
Fourier transform spectrometer we have observed a number
of infrared lines in the region between 5000 and 2000 cm^{-1}.
Several of these lines are known to be due to H_2
(transitions between various excited electronic states) but
a good number of the lines are unidentified. In order to
ascertain whether some of these unidentified lines are due
to H_3^+ one must either have reliable predictions or
differentiate by discharge conditions or by electromagnetic
deflection. We find that some of the unidentified lines
are much weaker in the anode glow than in the cathode glow.
Three years ago Carney and Porter (1976) made some
predictions about the theoretically expected infrared
spectrum. We find that the strongest predicted lines
agree with those observed infrared lines that show
considerable difference between the cathode and anode glow.
It would be hasty to consider this as proof of the
observation of the spectrum of H_3^+ since there are quite a
number of H_2 lines also. We either have to observe
complete bands allowing the use of the method of combination
differences for identification or we have to look at an
electronically deflected beam of H_3^+ ions. Such
experiments are now in preparation.

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DISCUSSION FOLLOWING HERZBERG

Hollenbach: Although grain composition may vary from place to place, I would think the correlation of diffuse bands with A_v more likely if the bands were caused by grains; molecular abundances generally are very sensitive to parameters such as gas density and radiation fields along the line of sight.

Herzberg: The references I have quoted, and several others, suggest considerable difficulty for that explanation.

Geballe: What type of H_2 lines might be contaminating the infrared spectrum of H_3^+ ?

Herzberg: The H_2 lines in question represent transitions between several excited states of H_2, for example E-B.