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Theoretical Studies of Interstellar Radicals and Ions

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I. Introduction

Molecular astrophysics is at present dominated by radioastronomy. A considerable number of interstellar molecules have been detected in the past 10 years by radio-frequency and microwave observations. Prior to 1968, the only species known to be present in space were simple diatomic molecules: CH, CN, CH^+, and OH. However, after the discovery of NH_3[1] and H_2O[2] in 1968, and H_2CO[3] in 1969, other polyatomic molecules have been detected, including several simple organic compounds such as methanol[4] (CH_3OH), formic acid[5] (HCOOH), and acetonitrile[6] (CH_3CN).

More recently, polyatomic free radicals such as C_2H,[7] C_3N,[8,9] and C_4H[9,10] have been identified, and polyatomic ions such as HCO^+ [11,12] and N_2H^+ [13–15] have been detected. In the laboratory, these species typically have lifetimes of the order of a few microseconds. In interstellar space, however, collisions are infrequent, and they may have lifetimes of several days. Astrophysical observations are, therefore, important because they provide information not only about interstellar processes, since radicals and ions may play a very important role in the formation of interstellar molecules, but also about terrestrially important reactive intermediates which are difficult to study in the laboratory.

The major obstacle to using astrophysical data to obtain information about such radicals and ions is the difficulty of identifying the interstellar spectrum without prior laboratory measurements. Because of the lack of experimental data, the assignment of spectra has relied, to a considerable extent, on ab initio quantum mechanical studies of molecular structure. Indeed, such calculations played a key role in the identification of HCO^+,[16,18] N_2H^+,[14,19] C_3N,[9] C_4H,[9] C_2H,[20–23] and HNC. Experimental studies have since confirmed the assignments for HCO^+,[24] N_2H^+,[25] and HNC.[26,27]

In this article, a description of the role which theoretical studies have played in the assignment of interstellar radio and microwave spectra of polyatomic radicals and ions will be given. Future studies in this area will be outlined. In radioastronomical studies we observe rotational transitions in molecules. Theoretical techniques cannot at present or in the near future hope to match the precision achieved in laboratory microwave experiments. It is therefore in the study of species which are highly reactive and short lived in the laboratory that theoretical computations are valuable. The review is divided into three main parts: a general discussion of molecules in space; an outline of the philosophy which we suggest should be adopted in theoretical work on potential interstellar molecules; some examples, both of molecules which have been detected in space and of molecules which we hope will be identified in the near future, are discussed.

Stephen Wilson obtained his B.Sc. in chemistry and Ph.D. in theoretical chemistry from The University of Bristol in 1971 and 1974, respectively. He undertook research on the electron correlation problem as a postdoctoral fellow at The Johns Hopkins University. As a National Academy of Sciences–National Research Council Resident Research Associate at NASA's Goddard Institute for Space Studies, he became interested in the application of quantum mechanical methods to possible interstellar radicals and ions. He maintains this interest while investigating new approaches to the molecular electronic structure problem at S.R.C.'s Daresbury Laboratory in Cheshire.

II. Molecules in Space

A. General Remarks

Most extraterrestrial molecules have been seen only in our own galaxy although CO, for example, has been detected in external galaxies. A large fraction of the mass of the galaxy is contained in interstellar clouds, and a substantial fraction of these clouds is molecular in character. Molecules containing H, C, N, O, Si, and S have been identified. Ultimately, the overall cosmic abundances of the elements constrain the molecular abundances. The relative abundances of the most common elements are roughly 0.9 H, 0.1 He, 0.001 C, N, and O, and 0.0001 Mg, Al, Si, S, and Fe. Beside the common isotopic versions, molecules have been observed with one or more of the rarer isotopes D, ^{13}C, ^{17}O, ^{18}O, ^{15}N, ^{33}S, and ^{34}S. The molecules range in size from simple diatomic species to HC_9N. The molecular clouds often correspond to areas of the sky which have a diminished number of visible stars. These darkened areas are generally believed to be regions of high dust density. The molecule and dust clouds are basically coextensive. The dense dust clouds (often called "dark" or "black" clouds) have a unique combination of conditions propitious for molecule survival in an otherwise seemingly hostile environment. High-energy radiation (cosmic rays, X-rays, etc.) which can destroy a molecule by ionization or dissociation and which permeates the general interstellar medium may be significantly attenuated by the large dust-column densities associated with the molecular clouds. The more complicated molecules generally tend to be seen in a limited type of region. Molecules can be used as sensitive probes of interstellar conditions. Information about the constitution, location, and velocity of interstellar clouds can be gained by detecting and measuring their position and the amount by which their spectral features are Doppler shifted. Analysis of the intensity of signals can yield information about the physical conditions within the clouds.

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B. Selection Effects

Various "selection" effects operate in the detection of interstellar molecules by radioastronomical techniques. These selection effects arise both from the basic quantum theory of molecules and from observational conditions imposed on the present-day astronomer.

(i) The molecule must, of course, have a dipole moment for its rotational spectrum to be observed. The presence of certain ions and radicals implies rather strongly that similar species which do not possess a dipole moment are present. For example, the presence of N_2H^+ almost certainly implies that N_2 is present; the detection of C_2H suggests that interstellar acetylene is present, and indeed this has been confirmed by infrared spectroscopic techniques. The requirement of a dipole moment is the only quantum mechanical selection effect which operates in these studies.

(ii) The signal must not be significantly attenuated by the earth's atmosphere. This is an observational constraint. It could be overcome by using orbiting telescopes. However, it does provide a real constraint on present-day observations.

(iii) The earth is probably a poor starting point for the study of molecular astronomy. It presents an unrepresentative chemical sample of the universe. For example, it has far less than the average proportions of H, He, and Ne. A molecule is more likely to be detected if its spectrum is well-known from laboratory studies. A cursory examination of the list of known interstellar molecules reveals that it is dominated by species which are known in the laboratory. Theoretical calculations can play an important role in overcoming this selection effect.

C. Interstellar Chemistry

Before discussing how theoretical calculations can help in assigning interstellar spectra, let us briefly discuss some of the models which have been proposed for molecule formation in space. It should be noted that the models do depend rather strongly on the particular molecules which have been discovered in space so far. The fact that a model of interstellar chemistry does not predict a particular molecule to be abundant in space should not exclude it from consideration when unassigned lines are discussed. However, models can lend support to molecule identifications. Ionization potentials, electron affinities, proton affinities, etc., give us an idea of how stable a particular species would be in space.

The reactions involved in interstellar chemical processes must have low activation energies. Ion–molecule reactions are thus believed to be of importance. Herbst and Klemperer[28] using ion–molecule reactions have proposed one of the most successful explanations of interstellar molecule abundances. However, it should be noted that they assume an initial concentration of H_2 and CO. Reactions on the surfaces of grains have also been considered. A difficulty here is that we do not know the composition of the grains. There is a further problem in that energy is required for the newly formed molecule to leave the surface of the grain. The work of Allen and Robinson[29] is of interest here. They suggest that the reactions take place on small grains and that the heat of formation of the molecule heats the grain sufficiently for the molecule to leave the surface. The physical processes which can occur in the gas-phase models include charge transfer, radiative association, electron–ion recombination (radiative recombination and dissociative recombination), photodissociation, and photoionization. Of course, it is possible that different reaction schemes are responsible for molecule formation in different regions of space. Furthermore, time-dependent effects may be important in explaining the observed abundances. More observational work on the distribution of interstellar molecules is required. A number of good reviews of interstellar chemistry have been published in recent years, and we refer the reader to these for further details.[30-37]

III. *Theoretical Studies of Potential Interstellar Molecules*

A. General Remarks

In principle, the spectrum of a molecule can be calculated from the corresponding Schrödinger equation. In practice, of course, it is necessary to introduce approximations in order to obtain a computationally tractable scheme.

The Born–Oppenheimer approximation, which results from the large disparity of the masses of the electrons and the nuclei in a molecule, enables the electronic and nuclear motions to be studied separately. The nuclear problem can be further subdivided to a good approximation in most cases into a translational part, a vibrational part, and a rotational part.

Rotational transitions are observed in radioastronomy. To a good approximation, the rotational transition frequencies for diatomic molecules are given by

$$\nu = 2B(J + 1)$$

where J is the rotational quantum number for the lower level involved in the transition and B is the rotational constant. The rotational constant depends on the moment of inertia of the systems which in turn depends on the equilibrium geometry. An improved rotational-term value may be obtained by allowing for distortional effects. An even better approximation results if one allows for the dependence of the rotational constant on the vibrational level being considered; the rotational constant is then given by

$$B_\nu = B_e - \alpha_e(\nu + \tfrac{1}{2})$$

The α_e's are vibration–rotation interaction constants. The generalization of these concepts to polyatomic molecules can be found in various standard texts.[38-44]

The equilibrium geometry of the molecule is determined by solving, within some approximation, the electronic Schrödinger equation (i.e., the equation for the electronic motion in the field of clamped nuclei). The reader is referred to one of the several texts available on the accurate solution of the electronic Schrödinger equation for a detailed description of the various approximations which can be invoked in order to render the problem computationally tractable.[45-47] This gives a potential-energy curve or surface, the minimum of which corresponds to the most stable geometry.

B. Theoretical Model Chemistry

In practical applications of the methods of theoretical chemistry there is much advantage in studying a wide range of problems at a uniform level of approximation. The results of all calculations at one level constitute what has been termed by Pople[48] a "theoretical model chemistry". The effectiveness of any model may be evaluated by comparing some of its details with real chemistry in areas where experimental data are available. If the results of such a comparison are favorable, the model acquires some predictive credibility.

To qualify as a satisfactory theoretical model chemistry, a method ideally should satisfy a number of conditions and requirements: (i) It should be "conventional". The method should have been applied to a wide variety of molecules and its strengths and weaknesses should be well documented. (ii) It should provied well-defined results for the energies of electronic states for any arrangement of fixed nuclei, leading to a set of continuous potential surfaces. (iii) The method should be such that the amount of computation does not increase too rapidly with the size of the system. (iv) The method should enable meaningful comparisions of molecules of different sizes to be made. Pople[48] refers to this property as "size consistency". The application of a method to an ensemble of molecules should give results which are additive for the energy and other properties. It should be noted that the widely used method of configuration interaction limited to single and double excitations does not satisfy this requirement.[49] (v) The calculated electronic energy should ideally be an upper or a lower bound to the true energy. (vi) The model should be the simplest possible which will afford the required results.

Calculations can provide estimates of stabilities, equilibrium geometries, rotation constants, hyperfine constants, dipole moments, etc. of postulated interstellar molecules, free radicals, and ions. For example, the Hartree-Fock model yields rotational frequencies which are reliable to 1 part in 100, while more sophisticated techniques are reliable to perhaps 2 parts in 1000.[42] While this accuracy does not approach that which can be obtained experimentally, it is often sufficient to exclude a postulated carrier. Empirical corrections can often be usefully made to the calculated results since theoretical methods usually differ from experiment in a uniform fashion for chemically similar species. In most of our work we have used the matrix Hartree-Fock model and incorporated empirical corrections to bond lengths when correlation effects are known, from studies of similar species, to have an important effect on structural parameters. Clearly, more attention should be given to structural parameters which determine the relative positions of the "heavy" atoms (carbon, nitrogen, and oxygen) than to the positions of hydrogen atoms, since the former have a much larger effect on the calculated rotation constants. Matrix Hartree-Fock calculations are inexpensive in comparison with the more sophisticated techniques of theoretical chemistry which are currently available, and they are very well understood. It is possible to study a range of related molecules by using this method and by comparing with experiment where possible give the results some predictive credibility. We feel that it is often more advantageous to study a series of related molecules, for example, a homologous series, including the species of potential astrophysical interest at a uniform level of approximation than it is to expand a great deal of computational effort on one species. In an extensive calculation[18] on the formyl ion, HCO^+, using limited configuration interaction, it was found necessary to make empirical corrections to the bond lengths determined from a parallel study of the experimentally known HCN molecule in order to obtain good agreement with the observed frequencies.

C. Fine and Hyperfine Structure

Fortunately, the spectra of many radicals and ions have characteristic multiplet fine and hyperfine structure. This can provide an invaluable "fingerprint" which enables a much more confident, and often positive, identification of an interstellar radical or ion to be made. For example, the identification of C_2H[7] and N_2H^+ [14] was initially based on theoretical estimates of their rotational frequencies. This was subsequently confirmed on the basis of fine and hyperfine constants which in the case of N_2H^+ were obtained theoretically. (These constants can be calculated with an accuracy of about 15% by using the Hartree-Fock model and about 5% if more refined techniques are employed.) Such splittings and the corresponding intensity ratios are often adequate to provide a firm identification. Calculated dipole moments are often invaluable in deriving column densities from astrophysical data.

A good example of the use of fine and hyperfine structure in the identification of a radical in space is provided by the ethynyl radical, C_2H.[7] Calculations[20,21] of the equilibrium structure of this radical allowed Tucker et al. to suggest that the ethynyl radical is responsible for the four lines which they observed in a number of galactic sources. The fine and hyperfine structure of the rotational spectrum of this radical enabled Tucker et al. to make a positive identification. Free C_2H has never been observed in the laboratory. It has been studied extensively by electron spin resonance, infrared, and optical spectroscopy while trapped in an inert gas matrix at liquid-helium temperatures.[50]

Identification of the ethynyl radical was based on the fact that the four new lines observed by Tucker et al. were due to the hyperfine splitting of the $N = 1 \rightarrow 0$ rotational transition. Since the spin-doubling and hyperfine interactions are very much smaller than the rotational energy, they can be treated by first-order perturbation theory and calculated from the Hamiltonian

$$\mathcal{H} = \nu S \cdot N + bI \cdot S + cI_z \cdot S_z$$

where N is the total angular momentum exclusive of spin, and S and I are, respectively, the electronic and proton spins with components S_z and I_z along the molecular axis. The hyperfine constants b and c were taken from the electron spin resonance experiments of Weltner and co-workers.[50] Tucker et al.[7] made a rough estimate of the spin-doubling constant ν on the basis of the experimental data. The hyperfine structure in the spectrum of the C_2H radical makes its identification in space quite convincing.

The discovery of the ethynyl radical in space has prompted a number of theoretical studies of this radical.

IV. Some Examples

A. General Remarks

We now discuss some of the molecules whose detection in space has relied to some extent on theoretical calculations and some of the species which have been suggested to be present in the interstellar medium for which theoretical studies have, therefore, been carried out. This discussion is necessarily selective rather than complete.

B. Protonated Nitrogen Molecule

Turner[13] reported three closely spaced interstellar lines near 93.175 GHz. Green, Montgomery, and Thaddeus[14] recognized that the structure of this triplet was characteristic of the hyperfine structure produced by the electric quadrupole interaction of a single nitrogen nucleus in the $J = 1 \rightarrow 0$ rotational transition of a linear closed-shell molecule. They suggested that the new species was the N_2H^+ ion. They argued that the inner nitrogen would lead to a hyperfine splitting which would be too small to be resolved in Turner's work and that the observed splitting was due to the outer nitrogen. To give some weight to these predictions, they performed matrix Hartree-Fock calculations to determine the equilibrium geometry, the electric-field gradients at the nuclei, and the permanent electric dipole moment. They used a double-zeta Gaussian basis set to determine the equilibrium geometry since such a basis is known to lead to good geometrical parameters in similar molecules. A larger Slater basis set, approaching the Hartree-Fock limit, was employed to determine the electric dipole moment and field gradient at the nuclei. The theoretical calculations formed the basis of a tentative identification of the N_2H^+ ion in space. They also provided the basis of a method for making a definitive identification of the carrier, namely, the resolution of the hyperfine splitting due to the inner nitrogen. This has now been done by Turner and Thaddeus.[15] Finally, the spectrum of this ion has been the subject of laboratory investigations by Woods and his group.[25] They obtained a spectrum which confirms the astrophysical assignment although, because of pressure broadening, the resolution of their spectrum does not approach that obtained by Turner and Thaddeus.

The N_2H^+ ion has been the subject of a number of theoretical studies.[19]

C. Cyanoethynyl Radical

Two emission-line doublets, which did not correspond to any known species, were observed by Guelin and Thaddeus[8] in the millimeter-wave spectrum of the infrared carbon star IRC+10216. They showed that the carrier was probably a molecule with a $^2\Sigma$ ground state. Since IRC+10216 does not contain the abundant interstellar ions HCO^+ and N_2H^+, the carrier is assumed to be neutral. By estimating the rotation constants for molecules of the type WXYZ, HWXYZ, and HWXYZH, where W, X, Y, and Z are carbon or nitrogen, they reduced the list of possible candidates to two species: the butadiynyl radical, C_4H, and the cyanoethynyl radical, C_3N. In linear molecules such as these, the splitting of higher rotational levels is equal to the spin-doubling constant, ν. Laboratory ESR work on trapped C_4H has been performed by Weltner and collaborators.[50]

Theoretical calculations[9] were performed on the butadiynyl radical, the cyanoethynyl radical, and also several related species in order to illustrate the reliability of the Hartree–Fock model in this context. Equilibrium geometries were calculated by using the matrix Hartree–Fock model, and from these theoretical values of the rotation constant were derived. Hyperfine interactions, which will cause additional structure in transitions among lower rotational levels, and electric dipole moments, which are required to infer column densities from observed intensities, were predicted. Double-zeta basis sets of Gaussian functions were used to determine equilibrium geometries while large Slater basis sets were employed in the calculation of hyperfine constants and dipole moments. From the theoretical bond lengths of the radicals, rotation constants of 4753 and 4955 MHz, respectively, for C_4H and C_3N were obtained. This should be compared with the rotation constant of 4948 MHz derived from the millimeter-wave spectrum of IRC+10216 by Guelin and Thaddeus. Thus, the butadiynyl radical is definitely excluded as the carrier of the observed lines. While the theoretical results do not unequivocally identify the lines as arising from the cyanoethynyl radical, they do lend rather strong support for this assignment. In fact, taken together with the known chemistry of IRC+10216, e.g., the strong cyanoacetylene emission, this identification becomes rather compelling. Laboratory studies would, of course, be conclusive.

Although the calculations indicated that the butadiynyl radical was not the carrier of the new lines, Wilson and Green[9] observed that "the fact that the simpler homologue, the ethynyl radical, has been observed, suggests that C_4H is also a potential interstellar species".

D. Butadiynyl Radical

More recently, the butadiynyl radical has been detected[10] toward IRC+10216. Four emission doublets have been identified as the $N = 9$–8, 10–9, 11–10, and 12–11 rotational transitions of the C_4H radical. The rotational constant derived from the astrophysical data, $B(0) = 4758.48$ MHz, is in excellent agreement with the previously reported theoretical value[9] of 4753 MHz. This agreement is to some extent fortuitous since vibration–rotation interaction effects were neglected in the theoretical study. However, we can have considerable confidence in the assignment since a series of related unsaturated hydrocarbons were also studied and good agreement with experimental data was obtained when available. This appears to be the first time that a theoretical calculation has been successfully used to predict characteristics of the microwave spectrum of a potential interstellar radical. Furthermore, Guelin et al.[10] comment that "Identification of C_4H considerably enhances the confidence that can now be placed in the identification of the similar radical C_3N". Although the lines of C_4H and C_3N are comparably strong in IRC+10216, because of the smaller dipole moment, C_4H seems to be the more abundant by roughly a factor of 4.

The detection[52] of the cyanoacetylenes, $H(C{\equiv}C)_nCN$ ($n = 0, 1, 2, 3, 4$), suggests that the homologous series of radicals $(C{\equiv}C)_nCN$ and $(C{\equiv}C)_nCCH$ for values of n greater than 1 may be present in space. CN and CCCN and CCH and CCCCH represent the first members of these series. The role which these radicals may play in the formation of long unsaturated molecules such as the cyanoacetylenes is an intriguing one and certain to be an area of future theoretical work. The extrapolation technique described recently by Oka[53] should provide reliable estimates of the rotation constants for these large radicals.

E. Metastable Organic Radicals

The detection of the cyanoethynyl radical in the molecular envelope of IRC+10216 is perhaps not surprising since HCN, CN, and HC_3N are fairly common species in space and are known to be particularly abundant in this particular star. Since hydrogen isocyanide, HNC, has been detected in space, it has been suggested[54] that the isocyanoacetylene molecule, HC_2NC, and the isocyanoethynyl radical, C_2NC, should also be searched for in space, particularly in the molecular envelope of IRC+10216 or a similar late-type carbon star. We have therefore performed calculations for these two molecules and for related species. Good agreement between theory and experiment was obtained from species for which experimental data are available.

It has recently been suggested[55] that many metastable isomers of small organic molecules may be present in dense interstellar clouds. Herbst and Green have made estimates of the abundance of various potential interstellar metastable organic radicals and ions. Often such species have not been studied experimentally, and theoretical calculations are of great value.

F. Radicals and Ions Containing Second-Row Atoms

A number of molecules have been detected in space in which the group 6 atom of the first row of the periodic table, oxygen, has been replaced by the corresponding second-row atom, sulfur. In addition to the diatomic species CO and CS and SiO and SiS, the polyatomic molecules H_2O and H_2S and H_2CO and H_2CS have been detected in space. Molecules such as SO and OCS, which contain both oxygen and sulfur, are also present. The thioformyl ion, HCS^+, and astronomically abundant formyl ion, HCO^+, are isovalent and we have suggested[56] that the former may be present in the interstellar medium. Matrix Hartree–Fock calculations were performed for CO, CS, HCO^+, and HCS^+. By comparison of the experimentally known bond lengths in the diatomic species with the calculated values, corrections were made to the lengths of the bonds between the heavy atoms in the ions. Vibration–rotation interaction constants for HCO^+ and HCS^+ can be taken from the work of Strey and Mills[57] on HCN and HCP, respectively. For the thioformyl ion a frequency of 43 116 MHz was derived for the $J = 1 \rightarrow 0$ transition. The $J = 2 \rightarrow 1$ and $J = 3 \rightarrow 2$ transitions are more likely to be observed astrophysically; they lie at 86.2 and 129.3 GHz. Limited configuration interaction calculations for the thioformyl ion have been reported by Bruna and co-workers.[58]

It is quite possible that a number of molecules will be detected in which first-row atoms are "replaced" by second-row atoms. We mention CSiH,[59] SiCH,[59] $HSiO^+$,[60] $HOSi^+$,[60] HSiN,[61] HNSi,[61] $HSiS^+$, $HSSi^+$, etc. as possibilities.

The discussion presented in this section has necessarily been selective. We briefly mention other species which have been studied theoretically and which appear to be likely candidates for detection in space. The isoformyl ion, HOC^+, has been investigated by Herbst et al.,[62] protonated carbon dioxide has been studied by Schor et al.,[63] and the HNO^+ and HON^+ ions have been the subject of recent calculations by Marian et al.[65] and by McLean et al.[64] $HNCH^+$, a possible intermediate in the formation of HNC from HCN, has been studied by Pearson and Schaefer.[66]

V. Concluding Remarks

It is now very probable that many polyatomic radicals and ions will be found in space, especially as radiotelescopes are improved. However, even a cursory listing of potential species reveals how little experimental information is known about most of them. It is clear that molecular structure calculations of the type described in this article will continue to play a significant role in the identification of new interstellar species. It seems that over the next few years we are going to see an increasing number of polyatomic ions and radicals being discovered in space. Such species not only are clearly of interest to the astrophysicist and astrochemist but also could have importance in the study of reactive intermediates which are difficult to observe in the laboratory.

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