THE ASTROPHYSICAL JOURNAL, 269:329–333, 1983 June 1

LABORATORY MEASUREMENTS OF ION-MOLECULE REACTIONS PERTAINING TO INTERSTELLAR HYDROCARBON SYNTHESIS

ERIC HERBST
Department of Physics, Duke University
AND
NIGEL G. ADAMS AND DAVID SMITH
Department of Space Research, University of Birmingham
Received 1982 November 8; accepted 1982 November 23

ABSTRACT

Measurements on a variety of three-body association reactions between hydrocarbon ions and molecular hydrogen in the presence of helium have been undertaken. The rate coefficients of most of the systems studied are vanishingly small ($<1 \times 10^{-30}$ cm^6 s^{-1}) even at 80 K. The results cast severe doubt on a recent gas-phase model of complex hydrocarbon formation in dense interstellar clouds in which radiative association reactions between hydrocarbon ions and molecular hydrogen play a key role. In addition to the three-body reactions, some two-body reactions between hydrocarbon ions and molecular hydrogen and some reactions between carbon ions (C^+) and hydrocarbon neutrals have been studied.

Subject headings: interstellar: molecules — laboratory spectra — molecular processes

I. INTRODUCTION

One of us (Herbst 1982*a*, *b*) has recently proposed a new ion-molecule pathway for the synthesis of complex interstellar hydrocarbon molecules (such as C_4H) and the cyanoacetylenes in dense interstellar clouds. The two major types of reactions utilized in the scheme are reactions between carbon ions (C^+) and neutral hydrocarbons and radiative association reactions between hydrocarbon ions and molecular hydrogen. Reactions between C^+ and hydrocarbons can increase the number of carbon atoms in the carbon chain of the hydrocarbon molecule. For example, in the well-studied reactions (Huntress 1977; Smith and Adams 1977; Schiff and Bohme 1979)

$$C^+ + CH_4 \rightarrow C_2H_3^+ + H; C_2H_2^+ + H_2$$
$$C^+ + C_2H_2 \rightarrow C_3H^+ + H ,$$

the carbon ion inserts itself into the hydrocarbon. Electron-ion recombination reactions can then produce neutrals with one more carbon atom than the precursor molecule, viz.,

$$C_2H_3^+ + e \rightarrow C_2H_2 + H$$
$$C_3H^+ + e \rightarrow C_3 + H .$$

Since carbon insertion takes place at the expense of a hydrogen atom (or atoms) and since electron-ion recombination also results in the loss of at least one hydrogen atom, the synthetic process is curtailed unless a mechanism exists to hydrogenate the hydrocarbon ions. Hydrogenation can occur via two types of reactions:

$$C_iH_j^+ + H_2 \rightarrow C_iH_{j+1}^+ + H ,$$
$$C_iH_j^+ + H_2 \rightarrow C_iH_{j+2}^+ + h\nu .$$

Unfortunately, for many hydrocarbon ions of interest the former process is endothermic and does not occur under normal interstellar conditions. The latter reaction is labeled radiative association; this type of reaction has been studied mainly by theoretical techniques (Herbst 1980*a*, *b*) but has recently been detected in the laboratory for the $CH_3^+ + HCN$ system (McEwan *et al.* 1980; Bass *et al.* 1981). Although radiative association reactions between hydrocarbon ions and molecular hydrogen have not been studied in the laboratory, several three-body association reactions in this category have previously been studied thoroughly. In particular, the reactions between $C^+ + H_2 + H_2$ (Johnsen, Chen, and Biondi 1980), $C^+ + H_2 + He$ (Adams and Smith 1981), and $CH_3^+ + H_2 + He$ (Adams and Smith 1981) have been measured and their rate coefficients observed to increase with decreasing temperature, in accordance with theory (Bates 1979; Herbst 1981). As discussed by Herbst (1980*a*), measurements of significant three-body reaction rate coefficients in the laboratory indicate that the analogous low pressure radiative association processes can occur efficiently under interstellar conditions.

Based on the limited amount of laboratory data then available on C^+ insertion reactions and hydrocarbon ion-molecular hydrogen three-body reactions, Herbst (1982*a*, *b*) proposed his model for complex molecule synthesis. One proposed route to molecules such as C_4H and HC_3N is depicted in Figure 1. As can be seen in the diagram, this model predicts that the cyanoacetylenes result from reactions between hydrocarbon ions and nitrogen atoms to produce precursor ions which then recombine with electrons. The model is based on two assumptions: (i) Reactions between C^+ and hydrocarbon neutrals include a significant insertion channel;

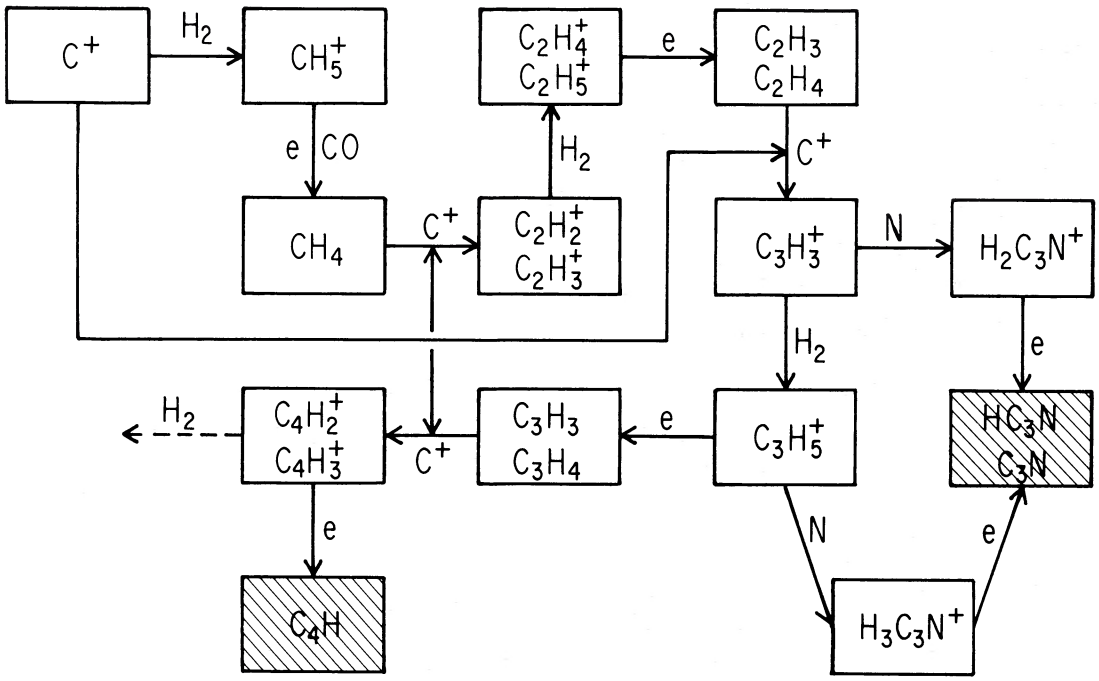

FIG. 1.—A block diagram of the ion-molecule pathway proposed by Herbst (1982*a*, *b*) for production of C_4H, HC_3N, C_3N, etc. via C^+ insertion reactions, radiative association reactions, and reactions with N atoms

and (ii) Hydrogenation of hydrocarbon ions via radiative association reactions with molecular hydrogen occurs efficiently at dense cloud temperatures.

The first group to test assumption (i) consisted of Bohme, Rakshit, and Schiff (1982) who studied the reactions between C^+ and C_2H_4, C_2H_6, C_3H_4 (allene and methyl acetylene), C_3H_6 (propylene), C_3H_8, and C_6H_6. These authors found the insertion channel to be a significant one ($>10\%$) for the unsaturated hydrocarbons C_2H_4, C_3H_4, and for the saturated hydrocarbon C_2H_6. Complementary work, reported here, also indicates that insertion does not occur to a large extent for larger saturated and slightly unsaturated species. However, the C^+ insertion reactions depicted in Figure 1 and used in Herbst's model have appreciable rate coefficients.

The major purpose of the present article is to present measurements relevant to the second assumption. A variety of three-body hydrocarbon ion-H_2 association reactions was studied with helium as the third body. With one notable exception ($C_2H_2^+ + H_2$), it was found that none of these reactions occurred at a measurable rate in the laboratory, even when measured at 80 K. Thus the inescapable conclusion is that Herbst's model for interstellar hydrocarbon and cyanoacetylene production is incorrect because the analogous hydrocarbon ion-H_2 radiative associations, crucial to his model, do not occur appreciably in the interstellar medium.

II. EXPERIMENTAL

The reaction systems studied and the results obtained are listed in Tables 1 and 2. The SIFT technique with its temperature variation capability has been discussed in detail previously (Adams and Smith 1976; Smith and Adams 1979). Briefly, the reactant ions are generated in a remote source, mass analyzed, and injected into fast-flowing helium gas. The ions are generated in an electron impact ion source containing either CO (for C^+), C_2H_4 (for $C_2H_2^+$, $C_2H_3^+$, $C_2H_4^+$), C_2H_6 (for $C_2H_5^+$, $C_3H_3^+$, $C_3H_4^+$, $C_3H_5^+$, $C_3H_7^+$), methyl acetylene C_3H_4 (for C_3^+, C_3H^+, $C_3H_2^+$) or n-C_4H_{10} (for C_4^+, C_4H^+). The reactant neutral gases are added to the helium carrier gas downstream from the reactant ion entry port, and the loss rates of the injected primary ions are measured as a function of the reactant gas flow rate by a downstream mass spectrometer detection system. The rate coefficients are obtained in the usual manner. Some disagreement exists between the product branching ratios obtained by us for the C^+ + hydrocarbon reactions and those obtained by Bohme, Rakshit, and Schiff (1982).

III. DISCUSSION

The negative results obtained for almost all of the hydrocarbon ion-molecular hydrogen association reactions (see Table 1) are surprising from a theoretical viewpoint. "Modified thermal" calculations (Bates 1979; Herbst 1980*c*, 1981) for a number of three-body association reactions have correctly predicted inverse temperature dependencies and have heretofore yielded rate coefficients within an order of magnitude of the experimental values. The type of agreement possible is shown in Table 3. In this table, the calculated rate coefficients for five three-body reactions between hydrocarbon ions and molecular hydrogen are compared with

TABLE 1

MEASURED REACTIONS OF HYDROCARBON IONS WITH H_2

System	T(K)	Rate Coefficient
1. $C_2H_2^+ + H_2 + He \rightarrow C_2H_4^+ + He$	80	7×10^{-27} cm^6 s^{-1}
2. $C_2H_3^+ + H_2 + He \not\rightarrow$	80	$<1 \times 10^{-30}$ cm^6 s^{-1}
3. $C_2H_4^+ + H_2 + He \not\rightarrow$	80	$<1 \times 10^{-30}$ cm^6 s^{-1}
4. $C_2H_5^+ + H_2 + He \not\rightarrow$	80	$<1 \times 10^{-30}$ cm^6 s^{-1}
5. $C_3^+ + H_2 \rightarrow C_3H^+ + H$	298	3.0×10^{-10} cm^3 s^{-1}
6. $C_3H^+ + H_2 \rightarrow C_3H_2^+ + H$	298	2.6×10^{-11} cm^3 s^{-1}
	80	1.4×10^{-10} cm^3 s^{-1}
7. $C_3H_2^+ + H_2 + He \not\rightarrow$	80	$<1 \times 10^{-30}$ cm^6 s^{-1}
	298	$<1 \times 10^{-30}$ cm^6 s^{-1}
8. $C_3H_3^+ + H_2 + He \not\rightarrow$	80	$<1 \times 10^{-30}$ cm^6 s^{-1}
	298	$<1 \times 10^{-30}$ cm^6 s^{-1}
9. $C_3H_4^+ + H_2 + He \not\rightarrow$	80	$<1 \times 10^{-30}$ cm^6 s^{-1}
10. $C_3H_5^+ + H_2 + He \not\rightarrow$	80	$<1 \times 10^{-30}$ cm^6 s^{-1}
11. $C_3H_7^+ + H_2 + He \not\rightarrow$	80	$<1 \times 10^{-30}$ cm^6 s^{-1}
12. $C_4^+ + H_2 \rightarrow C_4H^+ + H$	80	7×10^{-10} cm^3 s^{-1}
13. $C_4H^+ + H_2 + He \not\rightarrow$	80	$<1 \times 10^{-30}$ cm^6 s^{-1}

measured values at different temperatures. The first three systems show reasonable agreement between theory and experiment. These three systems had been studied at at least one temperature before Herbst (1982*a*, *b*) formulated his model. The other systems illustrate the large disagreement between theory and experiment observed for all other hydrocarbon ion-molecular hydrogen three-body systems. The reaction between $C_2H_3^+$ and H_2 in the presence of He possibly shows a direct rather than an inverse temperature dependence as predicted by theory. The reaction between $C_3H_3^+$ and H_2 in the presence of He has no observable rate coefficient; the discrepancy between experiment and theory is over three orders of magnitude even at 300 K. This marked disagreement exists for all of the three-body reactions we have studied for which only upper limit rate coefficients could be determined. Its cause is uncertain; the most facile explanation is the existence of activation energy barriers in the entrance channels. What is certain, however, is that the immeasurably small

TABLE 2

MEASURED REACTIONS OF C^+ IONS WITH HYDROCARBONS AT ROOM TEMPERATURE

		Distribution		Rate Coefficient (10^{-9} cm^3 s^{-1})	
System	Products[a]	This Work	BRS[b]	This Work	BRS[b]
1. $C^+ + C_2H_4$	$\rightarrow C_3H_3^+ + H$	60%	30%		
	$\rightarrow C_3H_2^+ + H_2$	20%	40%		
	$\rightarrow C_2H_4^+ + C$	10%	15%	1.7	1.3(.3)
	$\rightarrow C_2H_3^+ + CH$	5%	15%		
	$\rightarrow C_3H^+ + H_2 + H$	5%	...		
2. $C^+ + C_2H_6$	$\rightarrow C_3H_3^+ + H_2 + H$	50%	30%		
	$\rightarrow C_2H_3^+ + CH_3$	30%	30%		
	$\rightarrow C_2H_5^+ + CH$	10%	20%	1.7	1.6(.4)
	$\rightarrow C_2H_2^+ + CH_4$	10%	...		
	$\rightarrow C_2H_4^+ + CH_2$	...	20%		
3. $C^+ + C_3H_8$	$\rightarrow C_2H_3^+ + C_2H_5$	35%	25%		
	$\rightarrow C_2H_5^+ + C_2H_3$	...	35%		
	$\rightarrow C_3H_7^+ + CH$	30%	...		
	$\rightarrow C_3H_3^+ + CH_4 + H$	20%	20%	1.8	1.9(.5)
	$\rightarrow C_3H_8^+ + C$	10%	...		
	$\rightarrow C_4H_5^+ + H_2 + H$	5%	...		
	$\rightarrow C_2H_2^+ + C_2H_6$	...	20%		
4. $C^+ + n\text{-}C_4H_{10}$	$\rightarrow C_3H_5^+ + C_2H_5$	30%			
	$\rightarrow C_3H_7^+ + C_2H_3$	25%			
	$\rightarrow C_3H_3^+ + C_2H_6 + H$	20%	...	2.0	...
	$\rightarrow C_2H_3^+ + C_2H_6 + CH$	15%			
	$\rightarrow C_4H_9^+ + CH$	10%			

[a] Only ion products measured. Temperatures are 292 K for systems 1–3 and 294 K for system 4.

[b] Bohme, Rakshit, and Schiff 1982. Temperature is 296 K.

TABLE 3

COMPARISON OF CALCULATED AND MEASURED THREE-BODY RATE COEFFICIENTS k_{3B} ($cm^6\ s^{-1}$)

System	T(K)	Measured k_{3B}	Calculated k_{3B}
$C^+ + H_2 + H_2$.....	78	6×10^{-29} [a]	1.3×10^{-29} [b]
	300	3×10^{-29} [a]	0.61×10^{-29} [b]
$CH_3^+ + H_2 + He$....	82	1.5×10^{-27} [c]	6.4×10^{-27} [d]
	287	1.1×10^{-28} [c]	3.2×10^{-28} [d]
$C_2H_2^+ + H_2 + He$ ..	80	0.7×10^{-26} [d]	2.3×10^{-26} [d]
	300	1.2×10^{-27} [e]	2.1×10^{-27} [d]
$C_2H_3^+ + H_2 + He$ ..	80	$<1 \times 10^{-30}$ [d]	2.4×10^{-26} [d]
	300	$\lesssim 2 \times 10^{-29}$ [e]	1.1×10^{-27} [d]
$C_3H_3^+ + H_2 + He$ ..	300	$<1 \times 10^{-30}$ [d]	3.4×10^{-27} [d]

[a] Johnsen, Chen, and Biondi 1980.
[b] Herbst 1981.
[c] Adams and Smith 1981.
[d] This work.
[e] Adams and Smith 1977.

rate coefficients for three-body association imply very small radiative association rate coefficients at interstellar cloud temperatures.

We can estimate the analogous radiative association rate coefficients k_{RA} ($cm^3\ s^{-1}$) from the measured three-body rate coefficients k_{3B} ($cm^6\ s^{-1}$) in the following manner. The three-body process can be decoupled into a rapidly attained equilibrium between the reactants and an intermediate complex (Bates 1979; Herbst 1980*c*) followed by collisional stabilization of the complex. We can thus write k_{3B} as the following product:

$$k_{3B} = Kk_s\ , \tag{1}$$

where K is the equilibrium coefficient and k_s is the stabilization rate coefficient. This latter coefficient can be approximated by the collisional or Langevin value of about 1×10^{-9} $cm^3\ s^{-1}$. In an analogous manner (Herbst 1980*a*), k_{RA} can be written as

$$k_{RA} = Kk_r\ , \tag{2}$$

where k_r, the rate coefficient for radiative stabilization of the complex, is customarily in the range 10–1000 s^{-1} (Herbst 1982*c*). Thus, an upper limit value for k_{3B} at 80 K of 1×10^{-30} $cm^6\ s^{-1}$ yields an upper limit value for k_{RA} at this temperature of $1 \times 10^{-19\pm1}$ $cm^3\ s^{-1}$. Even assuming a strong inverse temperature dependence, values of k_{RA} at temperatures as low as 10 K are still insignificant. Consider $C_3H_3^+ + H_2$ as an example. "Modified thermal" calculations of the type performed by Herbst (1980*b*) predict that k_{RA} at 10 K is 2×10^{-13} $cm^3\ s^{-1}$. Assuming a T^{-2} dependence (Bates 1979; Herbst 1980*b*), the value inferred from our experiments is $<1 \times 10^{-17}$ $cm^3\ s^{-1}$. In the model of Herbst (1982*a*, *b*), values of k_{RA} in the range 1×10^{-13} to 1×10^{-14} $cm^3\ s^{-1}$ were necessary to obtain the observed abundances of molecules such as C_4H and HC_3N. Thus, the model cannot possibly yield sufficiently large C_4H and HC_3N abundances.

It is interesting to determine in the light of the new data which hydrocarbons can be produced via the combination of C^+ insertion reactions and hydrogenation reactions advocated by Herbst (1982*a*, *b*). The following sequence of reactions shows that species such as C_3H and C_4 can be produced efficiently:

$$C^+ + CH_4 \rightarrow C_2H_3^+ + H$$
$$C_2H_3^+ + e \rightarrow C_2H_2 + H$$
$$C^+ + C_2H_2 \rightarrow C_3H^+ + H$$
$$C_3H^+ + H_2 \rightarrow C_3H_2^+ + H$$
$$C_3H_2^+ + e \rightarrow C_3H + H$$
$$C^+ + C_3H \rightarrow C_4^+ + H$$
$$C_4^+ + H_2 \rightarrow C_4H^+ + H$$
$$C_4H^+ + e \rightarrow C_4 + H\ .$$

The reaction between C^+ and C_3H has not been studied. (It has been assumed throughout this work that H atom ejection is a favored pathway for ion-electron recombination reactions. See Green and Herbst 1979 for a discussion of this point.) The above reactions have been included in a total model of dense cloud chemistry currently being developed by Leung and Herbst (1983). Reactions between the generated hydrocarbon ions and atomic nitrogen might lead to molecular ions which are precursors to some observed interstellar carbon-nitrogen compounds. For example,

$$C_3H_2^+ + N \rightarrow C_3HN^+ + H\ ,$$
$$C_3HN^+ + e \rightarrow C_3N + H\ .$$

However, this approach does not lead to an efficient synthesis for HC_3N.

Since the model of Herbst (1982*a*, *b*) cannot explain the observed abundances of C_4H, HC_3N, and more complex species in TMC-1 and other clouds, is there another gas phase approach to their synthesis? A different ion-molecule approach to hydrocarbon production has been devised by Mitchell and Huntress (1979) and Schiff and Bohme (1979). This approach is illustrated in Figure 2 for C_4H production. Here, complex hydrocarbon ions are produced by condensation reactions between hydrocarbon ions and hydrocarbon neutrals (Huntress 1977), viz.,

$$C_2H_2^+ + C_2H_2 \rightarrow C_4H_2^+ + H_2$$
$$\rightarrow C_4H_3^+ + H$$
$$C_4H_2^+ + e \rightarrow C_4H + H$$
$$C_4H_3^+ + e \rightarrow C_4H + H_2\ .$$

The calculated abundances of the larger hydrocarbon neutrals in this scheme are exceedingly sensitive to the values of the smaller hydrocarbon (e.g., methane) abundances. Mitchell and Huntress (1979) estimated a fractional abundance of 1×10^{-8} for C_4H in dense clouds, in reasonable agreement with the observed value in TMC-1 (Guélin, Friberg, and Mezaoui 1982). Using somewhat different conditions and rate coefficients,

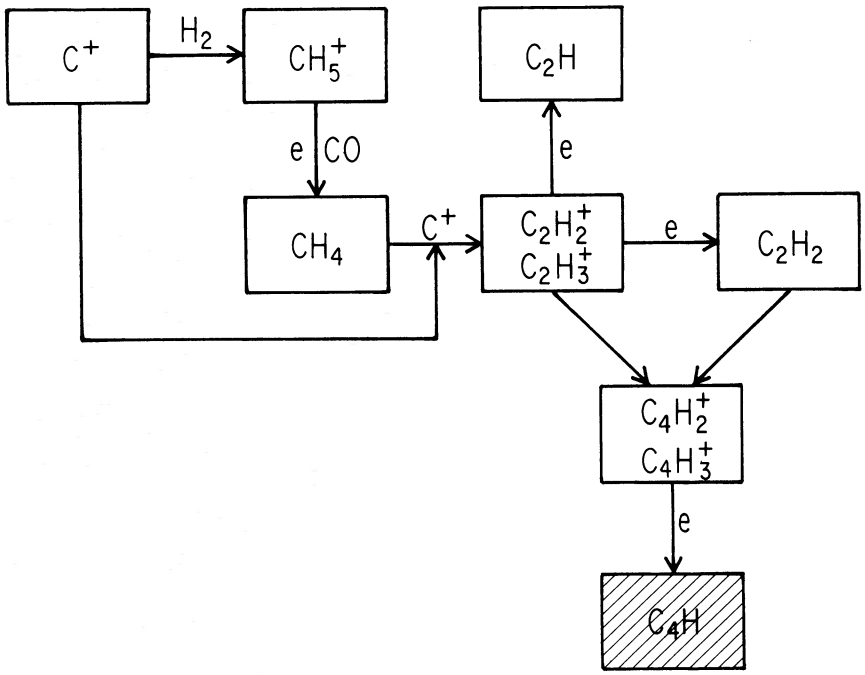

FIG. 2.—A block diagram of the ion-molecule pathway for C_4H production via hydrocarbon ion—hydrocarbon neutral condensation

Herbst (1982*b*) estimated a C_4H fractional abundance of $< 1 \times 10^{-10}$ via this approach. Thus, it is unclear whether or not C_4H and even more complex hydrocarbons can be formed in sufficient abundance by condensation reactions between smaller hydrocarbon neutrals and ions. Similarly, it is unclear whether or not hydrocarbon ions indicated by the schemes of Schiff and Bohme (1979) and Mitchell and Huntress (1979) in reactions with nitrogen atoms can account for the large abundances of HC_3N and other cyanoacetylenes detected in dense clouds.

One new observation that pertains to the ion-molecule synthesis of hydrocarbons is the discovery of large amounts of neutral carbon in dense clouds (Phillips and Huggins 1982). It is possible that carbon can be "fixed" by molecular ion-carbon atom reactions into methane and acetylene, thus increasing the abundances of these species and enhancing the prospect that hydrocarbon-hydrocarbon ion condensation can lead to the production of complex hydrocarbons and cyanoacetylenes. Calculations on this "fixation" are presently being undertaken.

E. H. wishes to acknowledge support for this research by the National Science Foundation via grant AST-8020321. N. G. A. and D. S. are grateful to the Science and Engineering Research Council (U.K.) for financial support for this work.

REFERENCES

Adams, N. G., and Smith, D. 1976, *Int. J. Mass Spectr. Ion Phys.*, **21**, 349.
———. 1977, *Chem. Phys. Letters*, **47**, 383.
———. 1981, *Chem. Phys. Letters*, **79**, 563.
Bass, L., Kemper, P. R., Anicich, V. G., and Bowers, M. T. 1981, *J. Am. Chem. Soc.*, **103**, 5283.
Bates, D. R. 1979, *J. Phys. B*, **12**, 4135.
Bohme, D. K., Rakshit, A. B., and Schiff, H. I., 1982, *Chem. Phys. Letters*, submitted.
Green, S., and Herbst, E. 1979, *Ap. J.*, **229**, 121.
Guélin, M., Friberg, P., and Mezaoui, A. 1982, *Astr. Ap.*, **109**, 23.
Herbst, E. 1980*a*, *Ap. J.*, **237**, 462.
———. 1980*b*, *Ap. J.*, **241**, 197.
———. 1980*c*, *J. Chem. Phys.*, **72**, 5284.
———. 1981, *J. Chem. Phys.*, **75**, 4413.
Herbst, E. 1982*a*, *Bull. AAS*, **14**, 605.
———. 1982*b*, *Ap. J.*, submitted.
———. 1982*c*, *J. Chem. Phys.*, **65**, 185.
Huntress, W. T., Jr. 1977, *Ap. J. Suppl.*, **33**, 495.
Johnsen, R., Chen, A. K., and Biondi, M. A. 1980, *J. Chem. Phys.*, **73**, 3166.
Leung, C. M., and Herbst, E. 1983, in preparation.
McEwan, M. J., Anicich, V. G., Huntress, W. T., Jr., Kemper, P. R., and Bowers, M. T. 1980, *Chem. Phys. Letters*, **75**, 278.
Mitchell, G. F., and Huntress, W. T., Jr. 1979, *Nature*, **278**, 722.
Phillips, T. G., and Huggins, P. J. 1982, *Ap. J.*, **251**, 533.
Schiff, H. I., and Bohme, D. K. 1979, *Ap. J.*, **232**, 740.
Smith, D., and Adams, N. G. 1977, *Ap. J.*, **217**, 741.
———. 1979, in *Gas Phase Ion Chemistry*, Vol. **1**, ed. M. T. Bowers (New York: Academic Press), p. 1.

NIGEL G. ADAMS and DAVID SMITH: Department of Space Research, The University of Birmingham, Birmingham, B15 2TT, England

ERIC HERBST: Department of Physics, Duke University, Durham, North Carolina 27706