HYDROCARBON ANIONS IN INTERSTELLAR CLOUDS AND CIRCUMSTELLAR ENVELOPES

T. J. MILLAR, C. WALSH, AND M. A. CORDINER

Astrophysics Research Centre, School of Mathematics and Physics, Queen's University Belfast, Belfast BT7 1NN, Northern Ireland;
Tom.Millar@qub.ac.uk, cwalsh13@qub.ac.uk, m.cordiner@qub.ac.uk

R. NÍ CHUIMÍN

Jodrell Bank Centre for Astrophysics, School of Physics and Astronomy, University of Manchester, Sackville Street, Manchester
M60 1QD, UK; Roisin.Ni-Chuimin@manchester.ac.uk

AND

ERIC HERBST

Departments of Physics, Chemistry and Astronomy, Ohio State University, Columbus, OH 43210-1106; herbst@mps.ohio-state.edu

ABSTRACT

The recent detection of the hydrocarbon anion C_6H^- in the interstellar medium has led us to investigate the synthesis of hydrocarbon anions in a variety of interstellar and circumstellar environments. We find that the anion/neutral abundance ratio can be quite large, on the order of at least a few percent, once the neutral has more than five carbon atoms. Detailed modeling shows that the column densities of C_6H^- observed in IRC +10 216 and TMC-1 can be reproduced. Our calculations also predict that other hydrocarbon anions, such as C_4H^- and C_8H^-, are viable candidates for detection in IRC +10 216, TMC-1, and photon-dominated regions such as the Horsehead Nebula.

Subject headings: astrochemistry — ISM: abundances — ISM: clouds — ISM: molecules — stars: carbon

1. INTRODUCTION

The recent detection by McCarthy et al. (2006) of C_6H^- in the carbon-rich asymptotic giant branch (AGB) star IRC +10 216 and in the cold, dense interstellar cloud TMC-1, with abundance ratios relative to C_6H of 0.01–0.1, indicates that anions may play a more significant role in interstellar physics and chemistry than heretofore believed.

The possibility that a relatively large fraction of molecular material in interstellar clouds might be in the form of anions was first suggested by Herbst (1981), who pointed out that carbon chain molecules and other radicals have large electron affinities, leading to high radiative attachment rates such as those measured by Woodin et al. (1980) with the attendant possibility of anion/neutral fractions on the order of a few percent. More recently, it has been recognized that polycyclic aromatic hydrocarbon (PAH) anions could soak up a significant fraction of the free electrons in interstellar clouds and alter the charge balance to a significant degree (Lepp & Dalgarno 1988a), as well as providing significant heating through photodetachment of electrons in diffuse clouds (Lepp & Dalgarno 1988b). Petrie (1996) has investigated the synthesis of CN^- by the dissociative attachment of MgCN and MgNC and other mechanisms, while Petrie & Herbst (1997) showed that C_3N^- could be detectable in interstellar clouds. The study of large hydrocarbon anions received some attention following the observation by Tulej et al. (1998) that absorption bands in several carbon chain anions coincided with several of the diffuse interstellar bands (DIBs). Subsequently, the formation of such species in diffuse clouds was studied by Ruffle et al. (1999), who showed, in particular, that C_7^- was unlikely to be a source for any DIB. Millar et al. (2000) considered the formation of hydrocarbon anions containing more than six carbon atoms in the carbon-rich circumstellar envelope of IRC +10 216 and showed that appreciable column densities could arise in the outer envelope.

2. CHEMICAL MODEL

The basic route to the formation of anions is electron radiative attachment:

$$X + e^- \rightarrow X^- + h\nu, \tag{1}$$

which has been discussed in the context of bare carbon chains by Terzieva & Herbst (2000). The rate coefficients of relevant processes have not been experimentally determined at low temperatures, and in this work we have used phase-state theory assuming s-wave attachment with radiative stabilization occurring by vibrational and electronic transitions (Terzieva & Herbst 2000). Table 1 contains some relevant attachment rate coefficients. The calculations of rates for these and other processes will be discussed in a separate paper (E. Herbst 2007, in preparation). For C_nH radicals, we find that radiative attachment occurs at the collisional rate once the number of carbon atoms is larger than five; for C_4H, the attachment efficiency is only around 1%. Barckholtz et al. (2001) have shown experimentally that neither carbon chain anions nor hydrocarbon anions react with H_2 but that they do so with H atoms. We have also included loss reactions of anions with C, C^+, $C_2H_2^+$ (in IRC +10 216), and photons, with all cation-anion rate coefficients taken to be 10^{-7} cm³ s⁻¹. For the photodetachment rates, some of which are shown in Table 1, we have assumed the cross section σ to depend on photon energy ϵ via the relation

$$\sigma = \sigma_0(1 - EA/\epsilon)^{0.5}, \quad \epsilon \geq EA, \tag{2}$$

where $\sigma_0 = 1.0 \times 10^{-17}$ cm² and EA is the electron affinity of the neutral molecule. Relevant electron affinities have been obtained from theoretical and experimental results (E. Herbst 2007, in preparation). The UV radiation field as described by Mathis et al. (1983) has been adopted. We have extended earlier models such as that by Ruffle et al. (1999), which included C_n^-, $n = 7$–23, and by Millar et al. (2000), which included

TABLE 1
SOME REACTIONS AND RATE COEFFICIENTS

Reactions	Products	α	β	γ
$e^- + C_4H$	C_4H^-	2.00E−9	−0.5	...
$e^- + C_5$	C_5^-	3.30E−8	−0.5	...
$e^- + C_5H$	C_5H^-	9.00E−10	−0.5	...
$e^- + C_6$	C_6^-	1.70E−7	−0.5	...
$e^- + C_6H$	C_6H^-	6.00E−8	−0.5	...
$e^- + C_7$	C_7^-	5.00E−7	−0.5	...
$e^- + C_7H$	C_7H^-	2.00E−7	−0.5	...
$e^- + C_8$	C_8^-	1.70E−7	−0.5	...
$e^- + C_8H$	C_8H^-	6.00E−8	−0.5	...
$e^- + C_9$	C_9^-	5.00E−7	−0.5	...
$e^- + C_9H$	C_9H^-	2.00E−7	−0.5	...
$e^- + C_{10}$	C_{10}^-	1.70E−7	−0.5	...
$e^- + C_{10}H$	$C_{10}H^-$	6.00E−8	−0.5	...
$C_4H^- + photon$	$C_4H + e^-$	1.80E−9	0.0	2.0
$C_5^- + photon$	$C_5 + e^-$	3.00E−9	0.0	1.5
$C_5H^- + photon$	$C_5H + e^-$	3.70E−9	0.0	1.5
$C_6^- + photon$	$C_6 + e^-$	1.30E−9	0.0	2.0
$C_6H^- + photon$	$C_6H + e^-$	1.50E−9	0.0	2.0
$C_7^- + photon$	$C_7 + e^-$	2.40E−9	0.0	1.5
$C_7H^- + photon$	$C_7H + e^-$	3.00E−9	0.0	1.5
$C_8^- + photon$	$C_8 + e^-$	1.10E−9	0.0	2.0
$C_8H^- + photon$	$C_8H + e^-$	1.40E−9	0.0	2.0
$C_9^- + photon$	$C_9 + e^-$	1.60E−9	0.0	2.0
$C_9H^- + photon$	$C_9H + e^-$	2.00E−9	0.0	2.0
$C_{10}^- + photon$	$C_{10} + e^-$	1.00E−9	0.0	2.0
$C_{10}H^- + photon$	$C_{10}H + e^-$	1.40E−9	0.0	2.0

NOTE.—For electron attachment, $k = \alpha(T/300)^\beta$ in units of cm^3 s^{-1}; for photodetachment, $k = \alpha e^{-\gamma A_v}$ in units of s^{-1}.

C_nH^-, $n = 7$–23, down to anions containing four carbon atoms following the determination of the microwave spectrum of C_4H^- by Gupta et al. (2007).

In addition to the reactions discussed above, we have included in the circumstellar envelope (CSE) and photon-dominated region (PDR) models radiative association between carbon chain anions and neutrals leading to carbon chains of up to 23 carbon atoms (Millar et al. 2000), while in the dark cloud models we have included reactions between anions and O atoms, with a rate coefficient of 10^{-10} cm^3 s^{-1}, unless specifically measured (Eichelberger et al. 2002).

3. RESULTS

3.1. Circumstellar Envelope

We model the carbon-rich AGB star IRC +10 216 using the numerical model developed by Millar et al. (2000) and Millar (2003). They modeled the formation of anions with more than six carbon atoms and showed that the anion radial distribution could extend beyond 10^{17} cm, and relative to their neutral analogs, abundance ratios approaching 0.1 (for C_7^-, for example) could be achieved. Some results of our present calculation, in which we have extended our species down to C_4H^-, are shown in Table 2 and Figure 1. Our results show that column densities of 1.0×10^{13} cm^{-2} for C_4H^- to 2.3×10^{13} cm^{-2} for $C_{10}H^-$ are achievable, with anion-to-neutral column density ratios of 0.008 for C_4H to around 0.3–0.4 for C_6H, C_8H, and $C_{10}H$. Note that although the electron attachment efficiency for C_4H is only around 1% that of C_6H and C_8H, C_4H^- has a relatively large column density since C_4H is more abundant. Both C_4H^- and C_8H^- are candidates for detection in IRC +10 216. In the region interior to a radial distance of 8×10^{16} cm, the main loss of anions occurs through reaction with H atoms, while mutual neutralization with C^+ dominates in $(1.8$–$13) \times 10^{17}$ cm. Elsewhere, photodetachment is the major loss route.

McCarthy et al. (2006) measured a C_6H^- column density of

TABLE 2
IRC +10 216 HYDROCARBON ANION CHEMISTRY MODEL RESULTS

Species	Column Density (cm^{-2})	Peak Abundance relative to H$_2$	Obs. Column Density (cm^{-2})	Refs.
C_4H	1.3×10^{15}	2.1×10^{-6}	$(2$–$9) \times 10^{15}$	1, 2, 3, 4
C_4H^-	1.0×10^{13}	1.3×10^{-8}	...	...
C_6H	5.7×10^{14}	1.2×10^{-6}	$(0.3$–$3) \times 10^{14}$	3, 4
C_6H^-	1.7×10^{14}	2.6×10^{-7}	3×10^{12}	5
C_8H	2.1×10^{14}	4.4×10^{-7}	5×10^{12}	4
C_8H^-	5.8×10^{13}	1.4×10^{-7}	...	
$C_{10}H$	5.8×10^{13}	1.3×10^{-7}	...	
$C_{10}H^-$	2.3×10^{13}	8.3×10^{-8}	...	

REFERENCES.—(1) Avery et al. 1992; (2) Dayal & Bieging 1993; (3) Kawaguchi et al. 1995; (4) Guélin et al. 1997; (5) McCarthy et al. 2006.

3×10^{12} cm^{-2}, approximately 60 times less than is produced in our model. Although the column density is overproduced, it is important to note that the column densities of the large hydrocarbon chains are very sensitive to the initial abundance of acetylene adopted in the model. This results from the fact that the most efficient method of growth is via the addition of C_2 units. For example, if the initial abundance of C_2H_2 is reduced by 5, the column density of C_6H is reduced by about 45, and that of $C_{10}H$ by 100. The anion column densities are not affected as much, typically reducing by about an order of magnitude, since less acetylene also leads to a reduction in the abundances of H atoms and C^+ in the envelope. The observed anion-to-neutral ratio is 0.01–0.1, where the range is due to the range of reported C_6H column densities (Kawaguchi et al. 1995; Guélin et al. 1997) but is in reasonable agreement with the calculated value of 0.3, given the uncertainties in the rates of anion formation (by radiative electron attachment) and destruction.

Finally, we note that the anion abundances can be greater than that of free electrons in the region around 5×10^{16} cm. This reflects the efficiency of carbon chain growth and electron attachment. A similar result is found in dark cloud models when PAHs are included (Lepp & Dalgarno 1988a).

3.2. Dark Clouds

Here we adopt parameters applicable to the cold dust cloud TMC-1 [$n(H_2) = 2 \times 10^4$ cm^{-3}, $T = 10$ K, $A_v = 10$ mag] and perform quasi–time-dependent modeling. The initial ele-
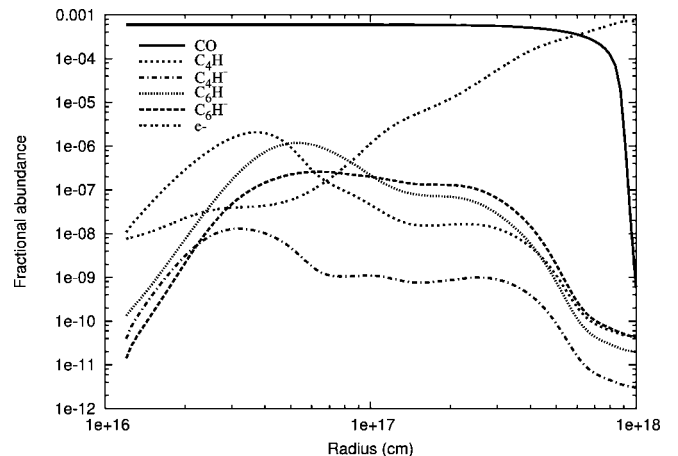

FIG. 1.—IRC +10 216 circumstellar chemistry model results of hydrocarbon and anion abundances (relative to the total number density), calculated as a function of distance from the center of the star.
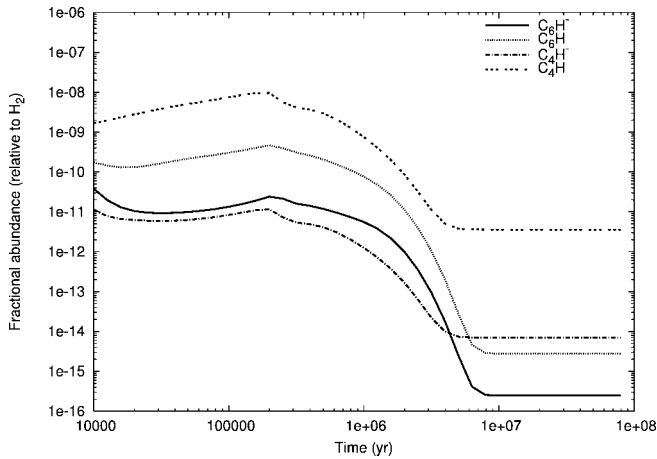
FIG. 2.—TMC-1 dark cloud chemistry model results of hydrocarbon and anion abundances (relative to H_2 density), calculated as a function of time.

mental abundances of C, N, and O relative to H are 7.30×10^{-5}, 2.14×10^{-5}, and 1.76×10^{-4}, respectively. Figure 2 shows the time-dependent evolution of the fractional abundances (with respect to H_2) of C_4H^- and C_6H^- and their corresponding neutrals from 10^4 yr, while Tables 3 and 4 present anion column densities and anion/neutral ratios respectively, at both early time (3.16×10^5 yr) and steady state ($>10^8$ yr). We adopt $N(H_2) = 10^{22}$ cm^{-2} in calculating the molecular column densities.

Steady state abundances are very low due to the incorporation of carbon into CO, but much better agreement occurs at earlier times in the evolution. The column density of C_6H^- produced in our model at early time (3.16×10^5 yr), 1.35×10^{11} cm^{-2}, is very close to that observed by McCarthy et al. (2006), 1×10^{11} cm^{-2}. We calculate the column density of the neutral C_6H at early time to be 2.58×10^{12} cm^{-2}, which is in good agreement with the observed value of 4.10×10^{12} cm^{-2} (Bell et al. 1999). The observed anion-to-neutral ratio is 0.025, which is in very good agreement with the calculated early-time value of 0.052, given the uncertainties in assorted rate coefficients.

3.3. Photon-dominated Regions

We have used the code developed by the Meudon group (Le Petit et al. 2006) with the additional hydrocarbon chemistry described above. For this model we assume a fixed temperature of 50 K and parameters representative of those in the Horsehead Nebula; i.e., $G = 60G_0$, where G_0 is the interstellar UV radiation field, $A_V = 10$ mag to the cloud center, and a total hydrogen density of 2×10^4 cm^{-3}. These models are steady state, which

TABLE 3
TMC-1 Hydrocarbon Anion Chemistry Model Results

Species	Column Densities (cm^{-2})			Ref.
	Early Time	Steady State	Observed	
C_4H	4.30×10^{13}	3.60×10^{10}	3.4×10^{14}	1
C_4H^-	5.58×10^{10}	6.99×10^7	...	
C_6H	2.58×10^{12}	2.78×10^7	4.1×10^{12}	2
C_6H^-	1.35×10^{11}	2.47×10^6	1.0×10^{11}	3
C_8H	7.76×10^{11}	1.63×10^6	2.2×10^{11}	2
C_8H^-	3.27×10^{10}	6.83×10^4	...	
$C_{10}H$	8.98×10^{10}	3.78×10^3	...	
$C_{10}H^-$	3.67×10^9	2.05×10^2	...	

REFERENCES.—(1) Guélin et al. 1982; (2) Bell et al. 1999; (3) McCarthy et al. 2006.

TABLE 4
TMC-1 Hydrocarbon Anion-to-Neutral Ratios
C_nH^-/C_nH

n	Early Time	Steady State	Observed[a]
4	1.30×10^{-3}	1.94×10^{-3}	...
6	5.23×10^{-2}	8.91×10^{-2}	2.50×10^{-2}
8	4.21×10^{-2}	5.42×10^{-2}	...
10	4.10×10^{-2}	5.42×10^{-2}	...

[a] McCarthy et al. (2006).

is achieved rapidly due to the enhanced UV field and fast photodestruction rates. The PDR models show that the anionic species formed can survive exposure to a high radiation field present in regions such as the Horsehead Nebula because, given the high electron abundance, the formation path of electron attachment is efficient enough to overcome the rapid photodetachment of the fragile anions. This high electron abundance at low to intermediate extinction can be inferred from the C^+ abundance in Figure 3, which also shows that significant abundances of the anions arise at low extinction ($A_V \sim 1.5$–3 mag). At low A_V, ~0.5–2 mag, the dominant loss of anions is through mutual neutralization with C^+ (and to a lesser extent through reactions with atomic hydrogen). Thus, since $n(C^+) = n(e)$ in this region, the anion/neutral abundance ratio depends on the ratio of the rate coefficients for electron attachment and mutual neutralization. For species with more than five carbon atoms, this leads to abundance ratios greater than unity; for smaller species, the ratio is less than 1. In fact, the abundances of the anions are, in some cases, larger than the neutral species. Relevant results are listed in Table 5. Most notably, C_8H^- and $C_{10}H^-$ are more dominant than the neutral species with fractional abundances over an order of magnitude greater than those of C_8H and $C_{10}H$.

Since the PDR model provides abundances perpendicular to the line of sight for a PDR seen edge-on, as is the case for the Horsehead Nebula, it is more appropriate to compare fractional abundances rather than column densities. The peak abundance of C_4H is consistent with observations of the Horsehead region made by Teyssier et al. (2004). Although the relative abundance of C_4H^- (3.5%) to its neutral analog is not as high as C_6H^- or C_8H^-, the higher abundance of the neutral species allows a significantly large absolute value of this anion to be formed. The C_6H^- anion has a peak abundance of 4.7 times that of the neutral species. The detection of C_6H in the Horsehead Nebula was reported by Teyssier et al. (2004), who calculated a peak
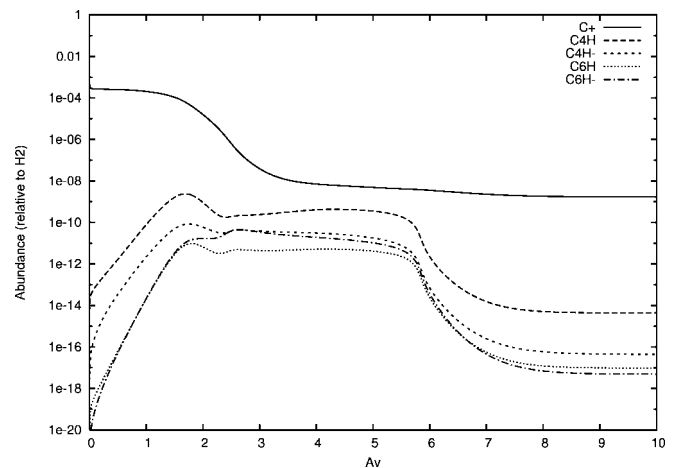

FIG. 3.—Horsehead Nebula PDR chemistry model results of hydrocarbon and anion abundances (relative to H_2), calculated as a function of A_V.

MILLAR ET AL.

TABLE 5

HORSEHEAD NEBULA HYDROCARBON ANION CHEMISTRY
MODEL RESULTS

Species	Peak Abundance relative to H_2	Obs. Peak Abundance relative to H_2[a]
C_4H	2.4×10^{-9}	$(3.0 \pm 1.2) \times 10^{-9}$
C_4H^-	8.4×10^{-11}	...
C_6H	9.6×10^{-12}	$(1.0 \pm 0.6) \times 10^{-10}$
C_6H^-	4.5×10^{-11}	...
C_8H	5.3×10^{-12}	...
C_8H^-	9.3×10^{-11}	...
$C_{10}H$	3.8×10^{-12}	...
$C_{10}H^-$	5.5×10^{-11}	...

[a] Teyssier et al. (2004).

abundance relative to H_2 of 1.0×10^{-10}, about 1 order of magnitude greater than calculated. It is possible that we are missing an important formation mechanism in this environment. One possibility is that hydrocarbon abundances are boosted by destruction of PAH particles, rather than being synthesized from smaller species. In any case, our anion/neutral ratios are independent of the mode of formation of the neutral.

4. CONCLUSION

We find that electron attachment to hydrocarbon molecules is very efficient for species containing more than five carbon atoms. The anions are created so efficiently that they can be abundant even in regions where they are destroyed rapidly by photons, such as CSEs and PDRs, and in dark clouds, despite the low fractional abundance of electrons. In particular, we find that anions such as C_6H^-, C_8H^-, and $C_{10}H^-$ can have abundances relative to their neutral analogs ranging from a few percent to greater than unity, while C_4H^-, although formed relatively inefficiently through electron attachment, can be observable in astronomical objects, given the large column densities of C_4H detected. In fact, as this Letter was being prepared, we became aware of a paper by Cernicharo et al. (2007) in which the detection of C_4H^- in IRC +10 216 is reported with a C_4H^-/C_6H^- column density ratio of $\frac{1}{7}$, compared to our calculated value of 1/17.

REFERENCES

Avery, L. W., et al. 1992, ApJS, 83, 363
Barckholtz, C., Snow, T. P., & Bierbaum, V. M. 2001, ApJ, 547, L171
Bell, M. B., Feldman, P. A., Watson, J. K. G., McCarthy, M. C., Travers, M. J., Gottlieb, C. A., & Thaddeus, P. 1999, ApJ, 518, 740
Cernicharo, J., Guélin, M., Agúndez, M., Kawaguchi, K., McCarthy, M., & Thaddeus, P. 2007, A&A, 467, L37
Dayal, A., & Bieging, J. H. 1993, ApJ, 407, L37
Eichelberger, B., Barckholtz, C., Stepanovic, M., Bierbaum, V., & Snow, T. 2002, in NASA Laboratory Astrophysics Workshop, ed. F. Salama (NASA CP-2002-21186; Washington, DC: NASA), 120
Guélin, M., Friberg, P., & Mezaoui, A. 1982, A&A, 109, 23
Guélin, M., et al. 1997, A&A, 317, L1
Gupta, H. C., Brünken, S., Tamassia, F., Gottlieb, C. A., McCarthy, M. C., & Thaddeus, P. 2007, ApJ, 655, L57
Herbst, E. 1981, Nature, 289, 656
Kawaguchi, K., Kasai, Y., Ishikawa, S.-I., & Kaifu, N. 1995, PASJ, 47, 853
Le Petit, F., Nehmeé, C., Le Bourlot, J., & Roueff, E. 2006, ApJS, 164, 506

Lepp, S., & Dalgarno, A. 1988a, ApJ, 324, 553
———. 1988b, ApJ, 335, 769
Mathis, J. S., Mezger, P. G., & Panagia, N. 1983, A&A, 128, 212
McCarthy, M. C., Gottlieb, C. A., Gupta, H. C., & Thaddeus, P. 2006, ApJ, 652, L141
Millar, T. J. 2003, in Asymptotic Giant Branch Stars, eds. H. J. Habing & H. Olofsson (New York: Springer), 247
Millar, T. J., Herbst, E., & Bettens, R. P. A. 2000, MNRAS, 316, 195
Petrie, S. 1996, MNRAS, 281, 137
Petrie, S., & Herbst, E. 1997, ApJ, 491, 210
Ruffle, D. P., Bettens, R. P. A., Terzieva, R., & Herbst, E. 1999, ApJ, 523, 678
Terzieva, R., & Herbst, E. 2000, Int. J. Mass Spectrom., 201, 135
Teyssier, D., Fossé, D., Gerin, M., Pety, J. Abergel, A., & Roueff, E. 2004, A&A, 417, 135
Tulej, M., Kirkwood, D. A., Pachkov, M., & Maier, J. P. 1998, ApJ, 506, L69
Woodin, R., Foster, M. S., & Beauchamp, J. L. 1980, J. Chem. Phys., 72, 4223