PHOTODETACHMENT SPECTRUM OF 1-C₃H₂: THE ROLE OF DIPOLE BOUND STATES FOR ELECTRON ATTACHMENT IN INTERSTELLAR CLOUDS

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ABSTRACT

The electronic spectrum of the linear propadienylidene anion 1-C₃H₂⁻ has been recorded at 50 K by resonance-enhanced two-photon detachment spectroscopy. This resembles the absorption spectrum to the dipole bound state involving bound-bound and bound-free transitions. The wavelength of the \( K = 1 \leftrightarrow 0 \) component for the origin and three vibrational bands match the weak and narrow diffuse interstellar bands. To explain the abundance of this carrier in interstellar clouds, the ratio of anions to neutrals is estimated for small polar molecules with high electron affinities using chemical considerations. An appreciable amount of anions can result in diffuse clouds because the electron attachment to polar molecules is enhanced via dipole bound states.

Subject headings: ISM: clouds — methods: laboratory — molecular data

1. INTRODUCTION

The role of anions in the interstellar medium (ISM) has not yet been clarified. Their abundance in dense interstellar clouds has been discussed by Sarre (1980) and Herbst (1981), but has been generally disregarded as a major factor. It has been argued, however, that in diffuse clouds large molecules with sufficient electron affinities (EA) will be present in an appreciable fraction as anions (Lepp & Dalgarno 1988a, 1988b; Lepp et al. 1988; Bakes & Tielens 1995; Salama et al. 1996; Dartois & d'Hendecourt 1997) despite the higher UV flux in this region. The \( H^- \) anion has been considered as a carrier of some of the diffuse interstellar absorption bands (DBIs) by Rudkjøbing (1969), although severe problems with this proposal have been pointed out by Snow (1973) and Herbst et al. (1974), who ruled out this candidate (as well as \( C^- \) and \( O^- \)) by comparison with laboratory spectra. Since the observation that in the electronic spectrum of \( C_7^- \) (Tulej et al. 1998) several stronger bands match weak DBIs, the abundance of anions appears to be viewed in a new light (Ruffle et al. 1999; Allamandola et al. 1999; McCall, York, & Oka 2000; Field 2000), although difficulties concerning the interstellar chemistry of anions remain.

Related to this are the observations of dipole bound states (DBS) of anions. These are electronic states close to the detachment threshold that have been shown to exist theoretically (Garrett 1971; Crawford 1971; Jordan & Wendolowski 1977) for neutral molecules with a dipole moment larger than about 2–2.5 D (Compton et al. 1996). The dipole field is able to bind an extra electron in a very diffuse orbital with a low binding energy. This makes them analogous to Rydberg states of neutral molecules, with the difference that the dipole field usually gives rise to only one bound anion state. They can be investigated experimentally by photoexcitation from low-lying valence states in the detachment threshold region (Zimmermann & Braumann 1977; Lykke, Mead, & Lineberger 1984). If no valence anion exists, a DBS can be the lowest electronic state of the anion. These can be formed directly in an appropriate source and studied by photoelectron spectroscopy (Hendricks et al. 1997) or by Rydberg electron transfer (Desfrancois et al. 1995). A comprehensive review of DBSs is given by Desfrancois, Abdoul-Carime, & Scherman (1996).

Anions with a polar neutral core can exhibit rich spectroscopic structure above and below the threshold (Mead et al. 1984; Lykke et al. 1987). The interaction leads to a loosely bound electron, and the geometry of the dipole bound anion is similar to that of the neutral molecule. The rovibrational states below the threshold are bound, while those above correspond to excited levels of the DBS, which can undergo autodetachment. These can be considered as rovibrational Feshbach states that can also be reached by electron capture and should provide a longer timescale for the electron to linger around the molecule before it is captured into an available unoccupied molecular orbital (Dessent, Kim, & Johnson 2000). In this paper we point out that DBSs could play an important role as intermediate states in the attachment of electrons to neutrals, similar to the mechanism studied in dissociative electron attachment experiments by Stepanovic, Pariat, & Allan (1999). They have also been discussed as “doorway states” for attachment into valence states of anions (Compton et al. 1996). In the ISM, the existence of long-lived DBSs could increase the attachment rate, increasing the abundance of anions.

An important class of molecules with a high dipole moment and high EA are the carbon chains, e.g., \( C_6H \) and \( C_6H_2 \), which are found in flames and discharge sources as neutrals as well as anions (Gerhardt & Homann 1990). Neutral unsaturated carbon chains, such as acetylenic radicals \( C_nH (n = 3–8) \), cyanopolynes \( HCN_N \), and cumulene carbenes \( H_2C_B \), have been identified in the circumstellar envelope of carbon-rich giant stars or dark molecular clouds (McCarthy et al. 1997b). These molecules have large dipole moments (> 4 D), rising with chain length, which makes their detection by microwave spectroscopy possible even if the relative densities are decreasing (McCarthy et al. 1997a).

The electronic transition from the \( ^2B_1 \) ground state of the propadienylidene anion, \( 1-C_3H_2^- \), to the \( ^2A_1 \) DBS has been observed in extensive and thorough studies by Yokoyama et al. (1996a, 1996b) at 500 K using high-resolution autodetachment spectroscopy. In this work, the electronic spec-
tron of 1-C₃H₂⁻ is reinvestigated, and a comparison with astronomical data and models is made. For the neutral C₃H₂ several isomers are relevant: cyclopropenylidene, C- C₃H₂, is the most stable, followed by propadienylidene, 1-C₃H₂, and the propargylene isomer, H₂C₃H. (Ikuta 1997). The neutral c-C₃H₂ molecule has been detected in the laboratory and in the ISM by millimeter-wave techniques (Thaddeus, Vrtilek, & Gottlieb 1985) and has been found to be ubiquitous (Matthews & Irvine 1985). Later, was-C₃H₂ was also detected by radio astronomy (Cernicharo et al. 1991). The neutral molecule has been detected in the ISM by millimeter-wave techniques (Lykke et al. 1987) with DIBs and formulated a dipole bound-state hypothesis for the carriers of the DIBs.

2. EXPERIMENTAL

The experimental approach has been described previously (Tulej et al. 1999). The anions are formed in a pulsed jet by a discharge of allene (0.5%) in argon. After entering a time-of-flight mass spectrometer through a skimmer, they are extracted by a ~3 kV pulse toward the detector. The mass-separated anion bunches are then intersected with a laser pulse (~10–20 ns). Its power is monitored by a photodiode.

Photodetachment (PD) spectra are recorded by scanning a dye laser pumped by a Nd:YAG laser (FWHM ~ 0.15 cm⁻¹). Shortly after the interaction region (~500 ns later) the anion bunches are reflected by a 45° mirror toward a microspherical plate detector to monitor the intensity and stability of the anion beam. The detachment process forms neutrals, which are not reflected but go through to a microchannel plate detector and yield the PD signal. To obtain the conditions for the resonant two-color photodetachment (R2CPD), a second laser (1064 nm) has been used to enhance the signal for bound states and states with long autodetachment lifetimes, which would otherwise not detach within the time window of our experiment (1–2 μs).

3. RESULTS

The electron affinity (EA) of 1-C₃H₂ has been measured as 1.794 ± 0.008 eV (Robinson et al. 1995). Ab initio theory predicts that c-C₃H₂ has a negative EA (i.e., the anion is less stable than the neutral molecule) and that the c-C₃H₂ is the most stable anionic isomer. It is 50 kJ per mol⁻¹ lower in energy than HC₃H⁻, which has a detachment energy greater than 1 eV (Ikuta 1997). The dipole moment of 1-C₃H₂ has been calculated (Gottlieb et al. 1993; Gutowski et al. 1997; Gutowski, Jordan, & Skurski 1998) to be greater than 4 D, and therefore a DBS must exist. This state has been observed by Yokoyama et al. (1996a, 1996b), and a full analysis of the observed spectrum was given. However, a comparison with astronomical absorption features is difficult because in their approach only the states above the detachment threshold are seen. While the spectra for the low-lying bands could in principle be simulated from these data, it was found advantageous to measure the spectrum at low temperatures (below 50 K) with the R2CPD technique, especially for the high-lying vibronic bands, where spectral congestion and lifetime broadening makes the analysis difficult.

Figure 1 shows a concatenated PD spectrum of 1-C₃H₂⁻ in the 590–702 nm region. The positions of the peaks maxima are collected in Table 1. The intensities of the peaks might not be reliable because different dyes had to be used. The spectroscopic constants of these four bands in the 2A₁(DBS) − 2B₁ transition have been inferred already in the high-resolution studies of Yokoyama et al. (1996b).

In Figure 2 the PD spectrum in the threshold region is displayed for different laser intensities. It is important to distinguish three cases to allow a comparison with the earlier work as well as with astronomical data. Trace a is recorded with low laser power, and only the rovibrational Feshbach states above the detachment threshold (i.e., EA) are seen in a one-photon process. These conditions are similar to the ones used by Yokoyama et al. for autodetachment spectroscopy, but the spectrum differs because they observed a large number of hot bands (~500 K), which are largely absent because of the lower temperature (~50 K) in the discharge source used here.

In trace b, the laser power is high enough that some two-photon processes are observed. The origin band is seen weakly. In scan c the conditions for resonance-enhanced two-laser photodetachment were achieved by using a

![Figure 1](https://example.com/figure1.png)

**TABLE 1**

<table>
<thead>
<tr>
<th>Laboratory (nm)</th>
<th>Assignment</th>
<th>DIB</th>
<th>FWHM (nm)</th>
<th>EW (mÅ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>699.37(7)</td>
<td>0⁰</td>
<td>699.32 (J)</td>
<td>0.096</td>
<td>116</td>
</tr>
<tr>
<td>678.81(7)</td>
<td>6⁰</td>
<td>678.87 (J)</td>
<td>0.087</td>
<td>7</td>
</tr>
<tr>
<td>648.97(1)</td>
<td>4¹</td>
<td>649.19 (J)</td>
<td>0.076</td>
<td>18</td>
</tr>
<tr>
<td>615.21(2)</td>
<td>2¹</td>
<td>615.115 (T)</td>
<td>0.144</td>
<td>0–15</td>
</tr>
</tbody>
</table>

**Note:** Wavelengths of the maxima of the K = 1 → 0 transitions for different vibronic bands in the 2A₁ → 2B₁ transitions of the propadienylidene, 1-C₃H₂⁻, anion and comparison with DIBs in the surveys of Jenniskens & Desert 1994 (J), Tuairisg et al. 2000 (T), and Weselak et al. 2000 (W).
second laser (1064 nm), which led to detachment after preparation of the excited state. The origin now appears as the strongest peak. This resembles a direct absorption spectrum if the excited states have similar detachment probabilities. Most likely, the intensity of the transition to the (bound) origin is still underestimated. Figure 3a shows the origin and Figure 3b the \( 4^1 \) vibronic band of the \( ^2A_i \rightarrow ^2B_j \) transition. At low rotational temperature, the \( K = 1 \rightarrow 0 \) \( Q \)-branches are expected to be the most intense lines. A simulation of the observed pattern leads to a temperature of 50 K.

The maxima of the \( 4^1 \) and \( 2^1 \) bands were calibrated to a precision of <0.02 nm using a simultaneously recorded iodine spectrum. The latter could not be obtained for the region of the origin and the \( 6^2 \) band, and the wavelength uncertainty is estimated to be <0.05 nm. The origin band has been simulated using the published constants (Yokoyama et al. 1996a), and the value obtained for the maximum of the \( K = 1 \rightarrow 0 \) transition is found to be within 0.04 nm of its wavelength in the present spectrum.

Table 1 also gives astronomical data from three DIB surveys (Jenniskens & Désert 1994; Tuairisg et al. 2000; Weselak, Schmidt, & Krelowski 2000). A DIB lies within 0.1 nm of the \( K = 1 \rightarrow 0 \) maximum of all of the four laboratory bands. However, all these DIBs are weak and narrow. Overlap by stellar and telluric features makes a precise determination of the parameters for such weak DIBs difficult. This might be the reason for the conflicting information in the surveys concerning the wavelengths and equivalent widths (EW). An EW ratio of \( \sim 6:1 \) for the 699.32 nm to the second strongest feature at 649.19 nm is inferred from the survey of Jenniskens & Désert (1994: the only one covering the range above 685 nm). The intensity ratio is difficult to determine from the laboratory spectrum (Fig. 1) because the \( 6^2 \) band belongs to a bound level in the upper state detectable only in a two-photon process, while the \( 4^2 \) band is associated with an autodetaching state.

Another uncertainty arises from the temperature of the molecular anion. Because of its large dipole moment, \( 1-C_3H_2^- \) should cool to the 3 K background temperature in interstellar clouds. This leads to slightly redshifted and narrower peaks than in the 50 K spectra presented. Simulation shows that below 5 K only the \( K = 1 \rightarrow 0 \) branches have significant intensity.

4. ASTROPHYSICAL IMPLICATIONS

In the discussion of the possible presence of anions in the diffuse interstellar medium, their stability and formation pathways must be considered. A stable concentration is maintained if the destruction by photodetachment \( (k_{\text{det}}) \), collisions with neutrals \( (k_{\text{coll}}[B]) \), and recombination \( (k_{\text{rec}}[I^+]) \) is balanced by their production by electron attachment \( (k_{\text{att}}) \). This can be tested qualitatively in a simple model similar to the one of Herbst (1981) and can be compared to related work concerning large molecules (Lepp & Dalgarno 1988a; Salama et al. 1996; Dartois & d’Hendecourt 1997). In general, the anion abundance in a diffuse medium compared to that of dense regions is increased because of the high electron densities and decreased because of higher photon flux. Therefore, a high electron EA (stability toward detachment as well as collision with neutrals) and a high electron attachment rate \( k_{\text{att}} \) will lead to a high relative anion abundance \( [A^-]/[N] \),

\[
\frac{[A^-]}{[N]} = \frac{k_{\text{att}}[e^-]}{k_{\text{coll}}[B] + k_{\text{det}} + k_{\text{rec}}[I^+]},
\]

where \( k_{\text{att}} \) for large molecules (such as polycyclic aromatic hydrocarbons [PAHs]) have been estimated by Omont (1986), Tielens (1993), and Allamandola, Tielens, & Barker (1989), and depend on their polarizability, assumed to be proportional to their size. A ratio of \( [A^-]/[N] > 2 \) for PAH molecules having more than 20 atoms was obtained by Dartois & d’Hendecourt (1997). This obtained ratio is comparable to those from the models of Lepp & Dalgarno (1988a), who derived a ratio of 0.15–1 for “large molecules,” and Salama et al. (1996), who found the anions to be dominant for PAHs with EAs \( \geq 1.1 \) eV. For small species these models do not yield high \( k_{\text{att}} \), and therefore yield no high anion abundances.
In the case of anions such as \( \text{C}_7^- \), the degree of dissociation of \( \text{H}_2 \) appears to be another critical parameter (Ruffe et al. 1999), because the H atoms lead to collisional detachment while the \( \text{H}_2 \) molecules are believed not to be reactive. Whether the collision leads to detachment or just H addition depends on the C-H bond energies and on the EAs of the species involved. For small molecules (such as \( \text{C}_3\text{H}_2 \)), equation (1) yields \( \frac{[A^-][N]}{N} \) ratios between 0.1 and 0.5 for the high relative electron densities and low temperatures in diffuse clouds if the attachment rate \( k_{\text{att}} \) is high (\( 10^{-7} - 10^{-6} \, \text{cm}^3 \, \text{s}^{-1} \)). Because the ratio \( \frac{[A^-]}{[N]} \) is directly proportional to the attachment rate \( k_{\text{att}} \) (eq. [1]), it is crucial for the anion abundance and is considered in the next section.

### 4.1. Attachment Process

The anions will be formed from neutrals by electron attachment or by the reaction of other anions with neutral species. The attachment process (with overall rate \( k_{\text{att}} \)) must therefore be split into two elementary steps (see Fig. 4): first, the formation of a temporary negative ion (TNI) \( k_f \), and second the relaxation of this complex to form a stable anion. The TNI is formed from a free electron and a neutral and is therefore above the threshold for detachment. The TNI can be stabilized via dissociation (\( k_{\text{DA}} \)) if energetically possible, or by radiation (\( k_r \)), which competes with autodetachment (the reverse process, \( k_{\text{AD}} \)). The overall attachment rate will then depend on all these processes:

\[
\frac{k_{\text{att}}}{k_{\text{DA}} + k_{\text{AD}} + k_r} = k_f = \frac{k_f}{k_{\text{DA}} + k_{\text{AD}} + k_r}.
\]

The second term in equation (2) is equivalent to the electron sticking coefficient \( \sigma \) in the treatment of Allamandola et al. (1989), if dissociation \( (k_{\text{DA}}) \) is not considered. The rate constant, \( k_r \), is assumed to be of the order of \( 10^{-3} \, \text{s}^{-1} \) (Herbst & Bates 1988; Terzieva & Herbst 2000; Petrie & Herbst 1997; Tielens 1993). To determine this sticking coefficient and the fate of the TNI, it is important to distinguish cases in which the internal conversion to a lower lying electronic state (\( k_{\text{IC}} \)) is fast and cases in which \( k_{\text{IC}} \) is small.

For the case of fast internal conversion to lower lying electronic states, the radiative relaxation is favored over detachment for large molecules with high EA because the lifetime of the TNI becomes larger with increasing density of states. The density of states for the TNI increases with EA and size, and therefore leads to higher \( k_{\text{att}} \), as has been pointed out by Allamandola et al. (1989). Petrie & Herbst (1997) have used phase-space theory to investigate the lifetime and stabilization of the initially formed collision complex (TNI) for \( \text{C}_3\text{N}^- \), and concluded that \( k_{\text{att}} \) will be small (\( \leq 2.2 \times 10^{-9} \, \text{cm}^3 \, \text{s}^{-1} \)) because detachment is faster than radiative stabilization. More recently, similar work on carbon chains (Terzieva & Herbst 2000) concluded that the attachment rate \( k_{\text{att}} \) can reach values of the order of \( 8.5 \times 10^{-7} \, \text{cm}^3 \, \text{s}^{-1} \) at 100 K. In this mechanism the anion formation is increased the slower the electrons in the ISM are and scales as \( T^{-1/2} \).

In the second case of slow internal conversion, a large \( k_{\text{att}} \) can only arise if the initially formed electronic anion state (resonance) is long lived. In electron-neutral scattering experiments, examples of such resonances are observed (Christophorou 1983). The cross sections for the formation of the TNIs are found to be especially high for polar molecules, increasing with decreasing electron energy (Rohr & Linder 1976) because of the long-range potential of the dipole (Clary & Henshaw 1987; Clary 1988).

An example by Bailey et al. (1996) showed how a Feshbach resonance in \( \text{O}_2^- \) mediates the dissociative electron capture of oxygen. Feshbach resonances have also been observed for carbon species such as \( \text{C}_2^- \) (Jones et al. 1980), and more recently \( \text{C}_5^- \) and \( \text{C}_6^- \) (Tulej et al. 2000; Lakin et al. 2000). It has been noted by Dessent et al. (2000) and Compton et al. (1996) that DBSs above the threshold (vibrational Feshbach resonances) can be these TNIs mediating the relaxation to a lower valence state of the anion. This is summarized in Figure 4. A similar observation has been made by Stepanovic et al. (1999) in the investigation of dissociative attachment \( k_{\text{DA}} \) to polar molecules, and they considered them acting as "doorway states" in the attachment process.

Stabilization for low \( k_{\text{IC}} \) can be studied on \( \text{I-C}_3\text{H}_2^- \) as an example, because the elaborate spectroscopic analysis of Yokoyama et al. (1996a, 1996b) revealed many details about the autodetachment and indicated long lifetimes \( (k_{\text{IC}})^{-1} + k_{\text{AD}}^{-1} \gg 5 \, \text{ns} \) for the low-lying rovibrational levels of the DBS. This autodetachment rate is so small that it could not be observed (by one photon excitation) within their time window for detection (3 \( \mu \text{s} \)) for states lying up to 400 \( \text{cm}^{-1} \) above the threshold. In view of the data in their Figure 8 (Yokoyama et al. 1996a), it appears reasonable that lifetimes of the lowest rovibrational Feshbach states are in the millisecond range and that radiative decay channels cannot compete efficiently with autodetachment \( (k_{\text{AD}} \leq k_{\text{IC}}) \). The reason for this long lifetime must be the low coupling efficiency to the continuum. To autodetach, the system must convert rotational or vibrational energy into electronic energy for the electron to escape. As discussed by Yokoyama et al. (1996a, 1996b), this is less efficient for the smallest rotational quantum numbers.

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**Fig. 4.**---Schematic view of the electron attachment and detachment processes considered. The ground states of the neutral \( ^1\text{A}_1 \), and the anion \( ^2\text{B}_2 \), are separated by the electron affinity EA. The lowest level of the DBS \( ^2\text{A}_1 \) is located below the neutral by \( E_{\text{bind}} = 195 \, \text{cm}^{-1} \). Rovibrationally excited levels of the DBS can lie above the neutral and are termed rovibrational Feshbach states. These states can also be formed by attachment of a low-energy electron \( (k_f) \) and can act as intermediates before relaxation to the ground state \( (k_r) \) or autodetachment \( (k_{\text{AD}}) \) takes place.
In both cases of slow and fast internal conversion it has been shown that there exist mechanisms that increase the lifetime of the TNI and lead to a high sticking coefficient $S$. In that case, $k_{\text{att}}$ is proportional to $k_j$, the initial attachment rate, which can become high for slow electrons and polar molecules because of the attractive $R^{-2}$ potential. The low-lying vibrations 6 and 9 and rotational $K_a$ and $N$ values yield a large number of potential resonant entrance states, making a high $k_{\text{att}}$ possible.

A high anion abundance in diffuse media can also be explained for small polar molecules with high EA with this mechanism. What seems to be a significant constraint on the validity for this approach might turn out to be relevant for the majority of molecules detected in the ISM so far. The majority of interstellar molecules detected by radio astronomy possess a large dipole moment (sufficient to support a DBS), increasing their detection probability. Most of the detected neutral molecules have a high EA (e.g., the carbon chains: $\text{C}_n$, $\text{C}_2\text{H}_2$, $\text{C}_2\text{N}$, $\text{C}_2\text{Si}$, $\text{C}_2\text{O}$, $\text{HC}_2\text{N}$), making the presence of their anionic counterparts likely.

These anions should exhibit intense optical transitions from the ground state to the DBS. Since the polar chains also possess high EAs (low-lying valence states), it can be assumed that in diffuse regions, where the electron density is higher, a considerable fraction of these molecules may be anionic. It has been pointed out that the valence to DBS transitions shows a clearly enhanced cross section (Desset et al. 2000). This leads to another interesting conclusion that has been brought up already by Sarre (2000): because the transitions from valence bound anions to their DBS are usually quite strong and their energy must be around their EA, some of these species are expected to have intense transitions in the visible range (1.5–3 eV), where the DIBs are found. The results presented here seem to support this, adding another example of possible DIB matches with laboratory spectra.

5. DISCUSSION AND CONCLUSION

The above considerations for enhanced electron attachment of polar molecules via DBS as “doorway states” to the stable anion suggest that some molecules may well be negatively charged in diffuse clouds. These results are similar to those derived for large molecules using a size-dependent polarizability, with an attractive $R^{-4}$ potential (Lepp & Dalgarno 1988a; Omont 1986). The present model proposes a mechanism through a specific class of resonances that explicitly takes into account the attractive $R^{-2}$ potential of polar molecules, and is therefore less size dependent. The relative anion abundance can be high, at least for polar molecules with high electron affinities covering a majority of the detected interstellar molecules. Since the polar hydrocarbon chains (e.g., $\text{C}_2\text{H}_2$, $\text{C}_2\text{H}_4$) fall into this category, it can be assumed that in diffuse regions, where the relative electron density is higher, a considerable fraction of these molecules may be anionic. Therefore, for diffuse clouds, negatively charged species may be found if the neutral species are present. So far, models of interstellar clouds (as well as models of molecule formation in flames and plasmas) include little or no anion chemistry. At least for diffuse clouds, these reactions appear to be important. Another set of relevant reactions are the collisions with neutral molecules (mainly H atoms), which can lead to detachment of the electron or H association, depending on the relative energetics.

An example for a strong electronic transition to a DBS is the PD spectrum of $\text{C}_2\text{H}_2$ in the visible range. The apparent matches with the DIBs are promising results to support the DBS hypothesis, even if more work should be undertaken to confirm the assignment. The relative intensities of the DB bands toward different stars should be studied to test whether they belong to the same carrier. The detection of $\text{C}_2\text{H}_2^-$ could explain the decrease of the $\text{C}_2\text{H}_2/\text{C}_2\text{H}_2$ ratio in diffuse media (Lucas & Liszt 2000; Cernicharo et al. 1999), because its negative EA can lead to depletion of this molecular structure upon electron detachment at the increased relative electron density in diffuse regions. For $\text{C}_2\text{H}_2^-$, an enhanced electron attachment can be expected because of its dipole moment of 3.3 D (Vrtilek, Gottlieb, & Thaddeus 1987). Once formed, this TNI could detach an electron or rearrange to the stable $\text{C}_2\text{H}_2^-$ anion, similar to the case of $\text{C}_2\text{H}$ (Petric & Herbst 1997). This would lead to the linear isomer and therefore decrease the $\text{C}_2\text{H}_2/\text{C}_2\text{H}_2$ ratio. Thus, the inclusion of reactions taking place on the negative ion potential surface in the chemical models in addition to the usual cation-molecule (Adams & Smith 1987) and neutral-neutral networks (Maluendes, McLean, & Herbst 1993) seems also to be worthwhile in this case. Other interesting reaction channels arise from dissociative attachment ($k_{\text{DA}}$) or collisions of anions with neutral molecules (mainly H atoms), which can lead to detachment of the electron or H association, depending on the relative energetics.

The column density of neutral $\text{c-C}_2\text{H}_2$ has been determined to be in the $10^{12}$–$10^{13}$ cm$^{-2}$ range, the $\text{C}_2\text{H}_2$ being 3–5 times less abundant, according to observations in the millimeter region (Cernicharo et al. 1999). A column density of 20% of this value for the $\text{C}_2\text{H}_2^-$ anion would be close to the detection limit even if the transition to the DBS is strong. This makes $\text{C}_2\text{H}_2^-$ also a good candidate for detection by radio astronomy.

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