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A CRITICAL EXAMINATION OF THE l-$C_3H_2^-$ SPECTRUM AND THE DIFFUSE INTERSTELLAR BANDS

B. J. MCCALL
Department of Astronomy, University of California at Berkeley, 601 Campbell Hall, Berkeley, CA 94720-3411; bjmccall@astro.berkeley.edu
AND
T. OKA, J. THORBURN, L. M. HOBBS, AND D. G. YORK
Department of Astronomy and Astrophysics, University of Chicago, 5640 South Ellis Avenue, Chicago, IL 60637
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ABSTRACT

It has recently been suggested by J. P. Maier's group that the origin band and three vibronic bands of the linear propadienylidene anion l-$C_3H_2^-$ match the diffuse interstellar bands (DIBs). We have examined the wavelength ranges in question using data from our ongoing DIB survey at the Apache Point Observatory. We find that the strongest DIB (λ6993) is not an acceptable wavelength match to the origin band of l-$C_3H_2^-$, based on high-resolution laboratory data. The nondetection of interstellar features corresponding to the $K = 2 \leftarrow 1$ and $K = 0 \leftarrow 1$ branches of para l-$C_3H_2^-$ also argues against the assignment of λ6993 to the $K = 1 \leftarrow 0$ branch of ortho l-$C_3H_2^-$. Two of the three DIBs that have been attributed to vibronic bands do not correlate in intensity with λ6993, providing further evidence against the assignment of this set of DIBs to l-$C_3H_2^-$.

Subject headings: ISM: molecules — line: identification — methods: laboratory — molecular data

1. INTRODUCTION

The mystery of the diffuse interstellar bands (DIBs), a series of absorption lines observed in the optical spectra of reddened stars, continues to puzzle the spectroscopic community. While most astronomers agree that the carriers of the DIBs are gas-phase molecules (Herbig 1995), intense efforts by astronomers and molecular spectroscopists have yet to yield any convincing match between the laboratory spectrum of any particular molecule and a group of the DIBs.

There were great hopes when J. P. Maier's group reported (Tulej et al. 1998) that their gas-phase spectrum of C_7^- appeared to match five DIBs in the catalog of Jenniskens & Désert (1994). While the match was tantalizingly close (McCall, York, & Oka 2000), subsequent laboratory work (Lakin et al. 2000) and astronomical observations (McCall et al. 2001) showed that the match did not stand up to the standards of high-resolution spectroscopy.

Recently, Maier's group suggested (Güthe et al. 2001) that l-$C_3H_2^-$ might be a DIB carrier, based on a comparison between their laboratory spectrum and the DIB catalogs of Jenniskens & Désert (1994), Tuairisg et al. (2000), and Weselak, Schmidt, & Krelowski (2000). We have compared the l-$C_3H_2^-$ spectrum to data from our DIB survey, and conclude that l-$C_3H_2^-$ is not the carrier of the DIBs noted by Güthe et al. (2001).

2. OBSERVATIONS AND DATA REDUCTION

The observations reported here are part of our long-term survey of the DIBs in a large sample of stars, as discussed by McCall et al. (2001). High-resolution ($R \sim 37{,}500$) visible (3700–10200 Å) spectra have been obtained with the Astrophysical Research Consortium (ARC) Echelle Spectrograph on the 3.5 m telescope at the Apache Point Observatory. Data reduction is performed using standard IRAF routines.[1] The data presented in this Letter are from a preliminary reduction of initial data and are part of the same data set used by McCall et al. (2001). The goal of our survey is to obtain spectra with a signal-to-noise ratio (S/N) greater than 1000 at 5780 Å. A more complete description of our DIB survey will be given in a future paper. A log of the observations used in this work is given in Table 1.

[1] The IRAF Data Reduction Guide for the ARC Echelle Spectrograph is available at http://www.apo.nmsu.edu/Instruments/echelle.

3. RESULTS AND DISCUSSION

3.1. *The l-$C_3H_2^-$ Spectrum*

The spectrum observed by Güthe et al. (2001) consists of electronic transitions from the vibrationless ground electronic state (0_0) of l-$C_3H_2^-$ (which has a symmetry $^2B_1$ in the C_{2v} point group) to various vibrational states (0^0, 6^2, 4^1, and 2^1) of the $^2A_1$ dipole-bound state. The strongest observed transition is the origin band (denoted 0_0^0) near 6994 Å. They also report three vibronic transitions: 6_0^2 near 6788 Å, 4_0^1 near 6490 Å, and 2_0^1 near 6152 Å. An energy level diagram of l-$C_3H_2^-$ is given in Figure 1.

The l-$C_3H_2^-$ anion consists of three carbon atoms in a chain, with two in-plane hydrogen atoms symmetrically off the chain at one end. The molecule is therefore an asymmetric top with C_{2v} symmetry. Based on high-resolution spectroscopy, Yokoyama et al. (1996) have determined the ground-state rotational constants to be $A = 9.73148$ cm^{-1}, $B = 0.34372$ cm^{-1}, and $C = 0.33151$ cm^{-1}. Because of the small mass of hydrogen, l-$C_3H_2^-$ is a nearly prolate symmetric top with $B \sim C$. (For the purposes of this work, we ignore the small spin-rotation and asymmetry splittings, which are generally less than 0.1 cm^{-1}.)

All of the transitions reported by Güthe et al. (2001) are type-(c) bands, which, in the limit of a prolate symmetric top, are perpendicular bands, with a selection rule $\Delta K = \pm 1$ (K is the projection of the rotational angular momentum N onto the molecular axis). Each band consists of a central dominant $K = 1 \leftarrow 0$ branch, with other $K + 1 \leftarrow K$ branches marching off to the blue, and $K - 1 \leftarrow K$ branches to the red (as seen in Fig. 3 of Güthe et al. 2001). The relative intensities of these branches are determined by the population of the various rotational levels as well as the Hönl-London factors.

Interstellar l-$C_3H_2^-$ can cool through dipole-allowed rotational transitions, so one might expect the rotational level populations to come into equilibrium with the cosmic microwave

TABLE 1
LOG OF OBSERVATIONS.

Star	$E(B-V)$	UT	Time (minutes)
ζ Oph	0.3	2000 Jun 10	1
HD 20041	0.33	2001 Feb 11	12
HD 41117	0.45	2000 Jan 24	25
HD 206267	0.51	2000 Aug 12	30
HD 210839	0.62	2000 Aug 13	9
HD 192639	0.64	2000 Aug 14	68
HD 50064	0.8	1999 Feb 23	60
BD +63°1964	0.85	2000 Oct 18	60
HD 147889	1.07	2000 Jun 10	60
HD 167971	1.08	2000 Jun 10	60
		2000 Jun 11	60
HD 183143	1.2	1999 May 31	30
		1999 June 11	40
Cyg OB2 5	1.7	2000 Aug 09	120
HD 229059	1.77	2000 Nov 18	30
		2000 Dec 01	25
Cyg OB2 12	3	1999 May 31	60

background radiation, at a temperature of 2.7 K. Since the A rotational constant corresponds to about 14 K, one might expect only $K = 0$ to be populated, and the spectrum to consist only of the central $K = 1 \leftarrow 0$ branch.

However, l-$C_3H_2^-$ contains two identical hydrogen nuclei, so it exists in two spin configurations, ortho and para. Because the ground electronic state is antisymmetric with respect to the exchange of the two protons, the K = even states are ortho and the K = odd states are para. Radiative transitions cannot interconvert the two spin configurations, so they can, at most, bring all the ortho molecules down to $K = 0$ and all the para molecules to $K = 1$. These two states would be expected to have a 3 : 1 population ratio, according to their spin statistical weights. Keeping this in mind, we expect the interstellar spectrum of l-$C_3H_2^-$ (if observed) to show the strong central $K = 1 \leftarrow 0$ branch, along with the nearby $K = 0 \leftarrow 1$ and $K = 2 \leftarrow 1$ branches, which should be approximately a factor of 6 weaker.

Within each K, the N-distribution is determined by a competition of collisional and radiative processes. We cannot simply assume equilibrium at 2.7 K, as in the case of CN, because collisional processes are faster (since l-$C_3H_2^-$ is charged) and radiative processes are slower (since the rotational transitions are lower in frequency). Adopting the collisional rate coefficients of Flower (1999) for HCO^+ -H_2 at $T = 30$ K (which should be similar to those of l-$C_3H_2^-$), and $\mu = 1.62$ D (the dipole moment of the isoelectronic H_2CCN; Hinchliffe 1979), we have calculated the rotational level populations for a density of $n = 100$ cm^{-3}, and these are listed in Figure 1. Of course, these populations are highly dependent on the adopted density: 90% of the population is in $N \leq 3$ for $n = 10$ cm^{-3}, $N \leq 5$ for $n = 100$ cm^{-3}, and $N \leq 12$ for $n = 1000$ cm^{-3}. However, the $K = 0 \leftarrow 1$ and $K = 1 \leftarrow 0$ branches are dominated by the sharp Q-branch, so the spectrum is fairly insensitive to the adopted density.

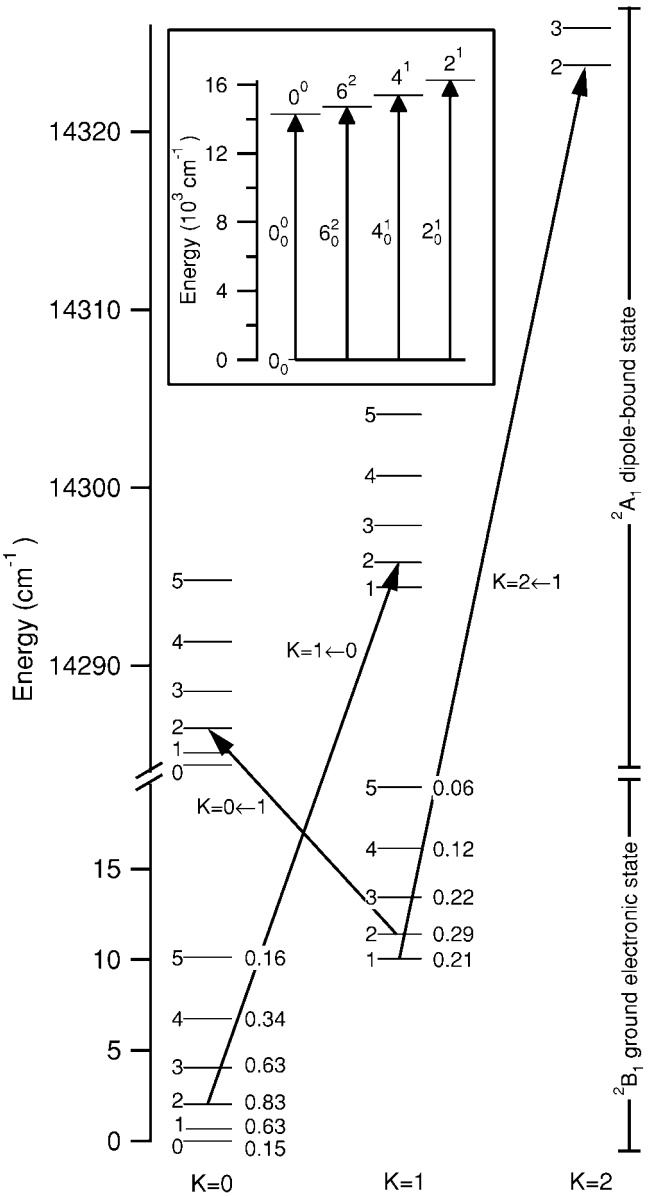

FIG. 1.—Energy level diagram of l-$C_3H_2^-$, in the prolate symmetric top approximation. The rotational quantum number N is given to the left of each rotational level. The relative populations of the levels in the ground electronic state are given to the right of each level, assuming an ortho-to-para ratio of 3 : 1 (see the text for details of the calculation). The arrows indicate the strongest transitions in each of the branches of the origin (0_0^0) band. The inset shows the vibronic structure only (ignoring the rotational structure), with the arrows indicating the origin band and the three vibronic bands considered in this work.

3.2. *The Origin Band*

The $K = 1 \leftarrow 0$ branch of the l-$C_3H_2^-$ origin band was observed by Güthe et al. (2001) at 6993.7 ± 0.7 Å. A diffuse band at 6993.2 Å has been reported by Jenniskens & Désert (1994). This wavelength region is contaminated by numerous lines of atmospheric water, which necessitates dividing the spectra of target stars by those of unreddened stars. Such divided spectra of six reddened stars are shown in Figure 2, along with simulations of the l-$C_3H_2^-$ spectrum obtained using the prolate symmetric top approximation described earlier. The interstellar spectra have been shifted in wavelength so that the K I line at 7699 Å is at zero velocity—that is, the spectra are displayed in the rest frame of the interstellar clouds.

Because the laboratory spectrum of Güthe et al. (2001) was obtained at a "high" temperature (~50 K) and has a fairly large (~0.7 Å) uncertainty in the wavelength calibration, it is best to compare the interstellar spectra with simulations based on the high-resolution spectroscopy of Yokoyama et al. (1996). These simulations accurately reflect the expected profile of the bands in interstellar conditions and have a substantially lower uncertainty in wavelength (considerably less than 0.1 Å).

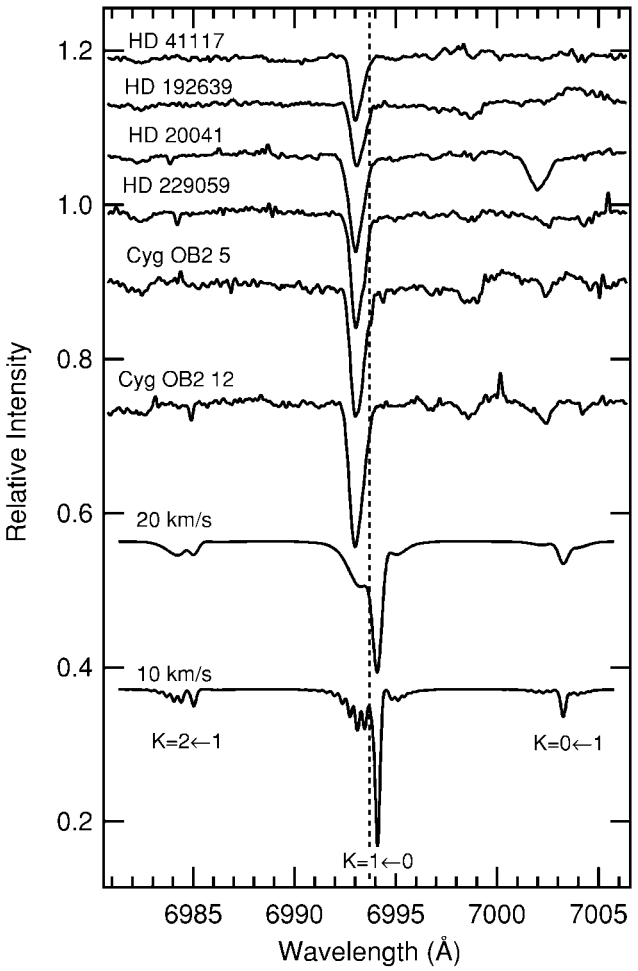

FIG. 2.—Spectra of the λ6993 DIB in several reddened stars (*upper traces*), compared with simulations of the $^2A_1 \leftarrow ^2B_1$ origin band (0_0^0) of l-$C_3H_2^-$ with an ortho-to-para ratio of 3 : 1. The reddened star spectra have been divided by spectra of unreddened stars (2 Lac and 15 Mon) in order to remove the many telluric water absorptions. The simulations assume Gaussian line widths of 10 and 20 km s^{-1} (the narrowest K I λ7699 lines in these stars have observed line widths of about 10 km s^{-1}). The dotted vertical line corresponds to the laboratory wavelength of Güthe et al. (2001). Note the lack of agreement between l-$C_3H_2^-$ and the DIB, in wavelength, in profile, and in the absence of the $K = 2 \leftarrow 1$ and $K = 0 \leftarrow 1$ components. All spectra have been shifted vertically from unity for clarity.

It is clear from this comparison that the λ6993 DIB cannot be assigned to l-$C_3H_2^-$. The DIB is not in agreement with either the central wavelength or the profile of the $K = 1 \leftarrow 0$ branch, and furthermore the $K = 2 \leftarrow 1$ and $K = 0 \leftarrow 1$ branches of the para spin configuration are not present in the interstellar spectra. Given the accuracy of the spectroscopic constants of Yokoyama et al. (1996), this lack of agreement rules out l-$C_3H_2^-$ as the carrier of this DIB. However, for the sake of completeness, we have also examined the three vibronic bands reported by Güthe et al. (2001).

3.3. *The Vibronic Bands*

Figure 3 shows the spectra of 13 reddened stars in the regions of the l-$C_3H_2^-$ bands, displayed in order of increasing central depth of λ6993. The spectra have been shifted in wavelength such that the dominant component of the interstellar K I line at 7699 Å is at zero velocity. However, in some cases (notably HD 167971 and 183143) there are multiple K I components, so that the DIBs do not necessarily line up perfectly. The $K = 1 \leftarrow 0$ wavelengths of Güthe et al. (2001) are displayed in Figure 3 as dotted vertical lines. (We have not performed simulations for the vibronic bands.)

The lowest (in frequency) reported vibronic band of l-$C_3H_2^-$ is the 6_0^2 band at 6788.1 ± 0.7 Å. Jenniskens & Désert (1994) cataloged a DIB at 6788.7 Å, and Weselak et al. (2000) reported the same DIB at 6788.66 Å. This DIB is clearly evident in Figure 3—in fact, it is the bluest member of a grouping of three DIBs of similar intensity. The discrepancy between the central wavelength of the DIB and the $K = 1 \leftarrow 0$ wavelength of Güthe et al. (2001) is within the quoted uncertainty of the laboratory measurement. We have not searched for the para branches since a band 6 times weaker than λ6789 would not be detectable given our S/N (the same is true for the other two vibronic bands as well).

The next reported vibronic band is 4_0^1 at 6489.7 ± 0.1 Å. Jenniskens & Désert (1994) list a DIB at 6491.9 Å, which is too far away for a match. Weselak et al. (2000) report a band at 6489.62 Å, and Tuairisg et al. (2000) report a band at 6489.29 Å. Our spectra clearly show the sharp DIB near 6492 Å and also a possible broad feature near 6489.5 Å. The latter feature is near the laboratory wavelength of the 4_0^1 band, but its strength is not correlated with that of λ6993.

Finally, there is the 2_0^1 band at 6152.1 ± 0.2 Å. Only Tuairisg et al. (2000) report a DIB near this position, at 6151.15 Å. This is clearly a much broader DIB than the others. Our spectra show some evidence for such a band, especially in the cases of Cyg OB2 12 and BD +63°1964. However, once again the strength of this DIB does not vary together with that of λ6993.

Even if one did assign λ6993 to the origin band of l-$C_3H_2^-$ (which we argue strongly against), the assignment of these other DIBs to the vibronic bands of l-$C_3H_2^-$ would require that they have a constant intensity ratio compared to λ6993. This is because the origin bands and the vibronic bands all arise from the ground vibrational state of the ground electronic state of l-$C_3H_2^-$ (see Fig. 1), and thus the relative intensities of these transitions are governed solely by the overlap of the upper-state vibrational wave functions with the ground-state vibrational wave function (i.e., the Franck-Condon factors). Even an unexpected rotational distribution could not alter this conclusion since these are all the same type of transition and obey the same selection rules—any change in the rotational populations would have the same effect on the intensities of all the bands.

Because of the nature of the photodetachment technique, the spectra of Güthe et al. (2001) do not provide useful information on the actual values of the relative intensities of the origin and vibronic bands. For this reason, we cannot predict how strong the vibronic bands should be. We do not wish to imply that this work constitutes strong evidence that l-$C_3H_2^-$ is not present in the interstellar medium but rather that these particular DIBs cannot be assigned to l-$C_3H_2^-$.

4. CONCLUSIONS

Based on a careful examination of spectra from our DIB survey, we find no evidence to support the suggestion of Güthe et al. (2001) that l-$C_3H_2^-$ is a carrier of any known DIBs. The $K = 1 \leftarrow 0$ branch of the origin band (which was proposed to correspond to λ6993) does not agree with the DIB in wavelength or profile. In addition, there is no sign of the corresponding $K = 2 \leftarrow 1$ or $K = 0 \leftarrow 1$ branches, which should be only about 6 times weaker if the ortho-to-para ratio is 3 : 1.

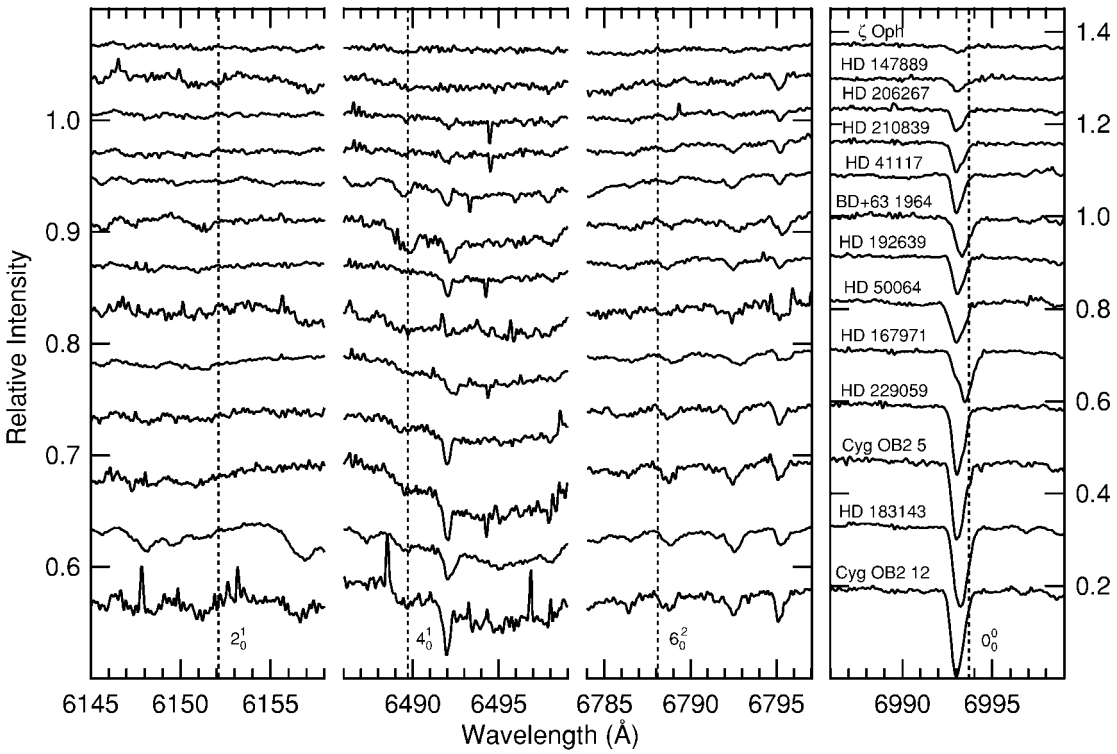

FIG. 3.—Spectra of the wavelength regions near the l-$C_3H_2^-$ bands observed by Güthe et al. (2001; their $K = 1 \leftarrow 0$ wavelengths are indicated by dotted vertical lines). Spectra have been shifted in wavelength so that the dominant component of the K I λ7699 line is at rest—in some cases (such as HD 167971) this leads to slight wavelength shifts among the DIBs. The regions near λλ6492 and 6993 have been corrected for telluric absorptions. Note that the panel for λ6993 has a different vertical scale. Spectra have been shifted vertically from unity for clarity.

The vibronic bands do not lend much support to the idea that l-$C_3H_2^-$ is a DIB carrier. The only possible match is the 6_0^2 band with λ6789. The other two DIBs that have been proposed to be assigned to l-$C_3H_2^-$ (λ6493 as 4_0^1 and λ6151 as 2_0^1) do not correlate in intensity with λ6993 (which would be assigned to the origin band). This lack of correlation rules out a common carrier for these bands in general and, thus, specifically rules out l-$C_3H_2^-$. In summary, there seems to be no evidence to support the suggestion that l-$C_3H_2^-$ is a carrier of the DIBs.

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