A NEW INFRARED BAND IN INTERSTELLAR AND CIRCUMSTELLAR CLOUDS: C₄ OR C₄H?

José Cernicharo¹ and Javier R. Goicoechea

Departamento Física Molecular, Instituto de Estructura de la Materia, CSIC, Serrano 121, E-28006 Madrid, Spain; cerni@astro.iem.csic.es, javier@isis.iem.csic.es

and

Yves Benilan

Laboratoire Interuniversitaire des Systèmes Atmosphériques, UMR 7583, CNRS, Universités Paris VII–XII, 94010 Créteil Cedex, France

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ABSTRACT

We report on the detection with the Infrared Space Observatory of a molecular band at 57.5 μm (174 cm⁻¹) in carbon-rich evolved stars and in Sgr B2. Taking into account the chemistry of these objects, the most likely carrier is a carbon chain. We tentatively assign the band to the νᵣ bending mode of C₄ for which a wavenumber of 170–172.4 cm⁻¹ has been derived in matrix experiments by Withey et al. An alternate carrier might be C₄H, although the frequency of its lowest energy vibrational bending mode, νᵣ, is poorly known (130–226 cm⁻¹). If the carrier is C₄, the derived maximum abundance is nearly similar to that found for C₃ in the interstellar and circumstellar media by Cernicharo et al. Hence, tetra-atomic carbon could be one of the most abundant carbon chain molecules in these media.

Subject headings: infrared: general — ISM: individual (Sagittarius B2) — ISM: lines and bands — ISM: molecules — line: identification — stars: individual (CRL 618, CRL 2688, IRC +10216, NGC 7027)

1. INTRODUCTION

Long carbon chain radicals have been detected in interstellar and circumstellar clouds through their pure rotational spectrum at radio wavelengths (C₃H, C₄H, C₂H, C₂H₃, H₂C₃, H₃C₄; Cernicharo et al. 1986, 1987; Guélin et al. 1987, 1997; Cernicharo & Guélin 1996). Polyynes such as C₂H₂, C₄H₂, and C₆H₂, and single atomic species such as benzene, have been detected in the proto–planetary nebula (PPN) CRL 618 (Cernicharo et al. 2001a, 2001b), supporting the idea that more complex carbon-rich molecules could be formed in space. However, the mechanisms allowing the growth of carbon-rich molecules are still poorly known, and the full set of molecules that could participate in the chemical reactions leading to the formation of large complex carbon-rich species has yet to be identified. Among these “building blocks,” the C₄ chains have attracted the interest of laboratory spectroscopists and astronomers. C₄ has been observed at optical wavelengths in the atmospheres of cool stars (see, e.g., Zuckerman et al. 1976), and it has been identified in the envelope of IRC +10216 through its νᵣ antisymmetric stretching mode in the mid-infrared by Hinkle, Keady, & Bernath (1988), who derived . This key species has recently been found in the interstellar medium (ISM; Cernicharo et al. 1996, 1997a; Cernicharo, Goicoechea, & Caux 2000; Giesen et al. 2001) through its νᵣ low-frequency bending mode (Schmuttenmaer et al. 1990) and in the diffuse interstellar clouds through its electronic transition near 4052 Å (Maier et al. 2001; Roueff et al. 2002). It has been suggested that C₄ could be involved in the formation of the diffuse interstellar bands (Douglas 1977; Clegg & Lambert 1982). ISM observations in Cernicharo et al. (2000) put a lower limit of 10⁻⁷ to the C₄ abundance. In addition, C₃ has been detected in the C-rich star IRC +10216 with an abundance ratio C₃/C₄ ≈ 10 (Bernath, Hinkle, & Keady 1989). Less is known about numbered carbon chains, but C₄ could well be a very abundant molecule both in C-rich evolved stars and in the ISM.

In this Letter, we report the detection of a blend of lines at 57.5 μm that we tentatively assign to the νᵣ bending mode of C₄. The feature has been observed in Sgr B2, IRC +10216, CRL 618, CRL 2688, and NGC 7027. We discuss the possibility that the carrier could be another different carbon chain, C₄H, although photodetachment experiments suggest that its lowest energy bending mode could be at higher frequencies (Taylor, Xu, & Neumark 1998).

2. OBSERVATIONS AND RESULTS

We have searched for the emission/absorption of the low-energy bending modes of polyatomic molecules toward interstellar and circumstellar clouds using the long-wavelength spectrometer (LWS; Clegg et al. 1996; Swinyard et al. 1996) on board the Infrared Space Observatory² (ISO; Kessler et al. 1996). Our main target for this search has been the C-rich evolved star IRC +10216. The LWS grating data of IRC +10216 were analyzed and modeled by Cernicharo et al. (1996). The data have been reprocessed following the last pipeline product (target dedicated time [TDT] 19800158). No significant differences have been found with the already published analysis. After identifying all the HCN (including several vibrational states) and CO lines, a conspicuous feature composed by a blend of several lines (see Fig. 1, top panel) was identified between 56 and 58 μm. These lines could not be assigned to any known species, and no other similar patterns were found in the ISO far-infrared spectrum of IRC +10216. We have checked for all pure rotational lines of light species that could be potentially abundant without success. Hence, the only possible explanation is that the feature

¹ Visiting Scientist, Division of Physics, Mathematics, and Astronomy, California Institute of Technology, MS 320-47, Pasadena, CA 91125.

² Based on observations with ISO, an ESA project with instruments funded by ESA member states (especially the PI countries: France, Germany, the Netherlands, and the United Kingdom) and with participation of ISAS and NASA.
For the planetary nebula NGC 7027, we have used all the LWS grating data taken by ISO (see Herpin et al. 2002 for details). The data for the PPN CRL 618 (TDTs 68800302 and 68800450) are those published by Herpin & Cernicharo (2000). For CRL 2688, a young PPN, the TDT 02101504 data have been used. A previous analysis of the ISO/LWS spectrum of this source has been presented by Cox et al. (1996).

All the spectra have been analyzed using the ISO spectrometer data reduction package ISAP. The data products correspond to version 10 of the pipeline. A polynomial baseline had to be removed from the final spectrum in each source. For some objects, this baseline removal is critical to correctly extract the shape and intensity of the absorption features. Owing to the large number of lines in Sgr B2M and N spectra, the determination of the continuum level is not obvious. For sources with emission lines, although baseline removal is less critical, the global behavior of detector SW2 does not follow the expected shape for continuum emission, and a polynomial of fourth degree has been removed after blanking the wavelength intervals where features above 5σ were present.

Figure 1 shows the 53–62 μm spectra of the selected sources. We have also analyzed the available observations for several other sources—O-rich stars, Orion, Sgr A, bright molecular sources, and even Mars—to check for possible instrumental effects. The new infrared feature was not detected in any of these sources. We have also examined the spectral response of the LWS-SW2 filter in order to check for possible instrumental contributions to the blend of lines found around 57 μm, but there is nothing at this wavelength (P. García-Lario 2002, private communication). Hence, we conclude that the blend of lines is real. The pure rotational lines of CO and HCN are indicated in the top panel of Figure 1. The model of Cernicharo et al. (1996) predicted a low flux for these high-J lines. Only in IRC +10216 are some of the CO lines (J = 43–44, 44–45, and 45–46) marginally detected at a 3σ level.

The observed band consists of a blend of at least four spectral lines or subbands (at 57.0, 57.6, 57.9, and 58.2 μm). There is an additional feature separated from the band at 56.15 μm that is detected in C-rich evolved stars but is less evident in Sgr B2N and M. The J = 47–46 line of CO could only make a modest contribution to this feature in C-rich evolved stars since other high-J CO lines are weak—even in IRC +10216. In Sgr B2M, this feature is blended with the absorption produced by NH (J = 9–8). The 56.15 μm feature could be one of the fine-structure lines of [S I] at 56.31 μm (P_1/2^1–P_1/2^1), but its companion [S I] (P_3/2^1–P_1/2^1) line at 25.249 μm is missing in all objects. The feature could also be the R(1) line of HD. However, it is unlikely to find such a high intensity for this line in evolved stars. We think that, if instrumental, the feature could arise from Uranus, the planet used as a calibrator for the LWS grating spectrometer. However, its intensity changes by more than a factor of 10 between NGC 7027 and IRC +10216 or CRL 618 (the continuum flux at 58 μm is nearly the same for NGC 7027 and CRL 618, 1.15 and 0.7 × 10^{-16} W cm^{-2} μm^{-1}, respectively, and 4 and 3 × 10^{-16} W cm^{-2} μm^{-1} for IRC +10216 and CRL 2688, respectively). Therefore, the 56.2 μm feature in IRC +10216, CRL 618, NGC 7027, and CRL 2688 cannot


corresponds to a bending mode of an abundant heavy molecule and most likely to a carbon chain. We searched for the same feature toward other objects selected from the same criteria of our previous searches of C_2, C_2H_2, C_3H_2, and benzene (Cernicharo et al. 1996, 1997a, 2000, 2001a, 2001b), i.e., IRC +10216, CRL 618, CRL 2688, NGC 7027, and Sgr B2 (among other sources).

For Sgr B2M, we have used the LWS grating spectra obtained during revolutions 287 and 494 (TDTs 28701401, 287012130, 287012131, and 49400302). Some of these data have been already presented (Cernicharo et al. 1997b; Gioioccoeca & Cernicharo 2001). All together, they represent a total of 32 individual scans. The feature at 57.5 μm is clearly present. There are many other LWS grating observations of Sgr B2 with a reduced number of scans. We have inspected all of them and, again, the feature appears in each individual scan. Sgr B2N was observed in the course of a fast mapping of the Sgr B2 star-forming region with the LWS, and only four scans are available (see Cernicharo et al. 1997b).

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<Diagram of observed ISO/LWS spectra toward the sources discussed in the text. The wavelengths of the CO lines J = 43–42 up to J = 49–48 and those of HCN J = 56–55 up to 64–63 are indicated by arrows in the top panel. For IRC +10216, CRL 2688, CRL 618, and NGC 7027, the continuum level has been removed. For Sgr B2N and Sgr B2M, the line over continuum flux ratio is shown. In all cases, the continuum has been derived from a polynomial fit to the spectra after removing all emission/absorption features above 3σ. The bottom panel shows the expected band shape for a transition 1Π–1Σ with A_{ll} = 4 cm^{-1}, intrinsic line width of 10 km s^{-1}, and spectral resolution, κ/Δκ, of 200.>
be explained alone by a possible instrumental contribution from the calibrator. Figure 1 shows that the 56.2 μm line follows the intensity of the 57–58 μm features. In the following, we will consider that all of them belong to the same molecular band.

Two additional features at 53.7 and 54.4 μm in the spectrum of IRC +10216 (labeled U1 and U2 in the top panel of Fig. 1), and another one at 52.89 μm (not shown), are also detected in NGC 7027 but not in the other sources. These three lines remain, so far, unidentified. The contribution of OH (Goicoechea & Cernicharo 2002) and the maximum possible contribution from H2O (J. Cernicharo et al. 2003, in preparation) to the spectra of Sgr B2N and M are indicated in the panel corresponding to Sgr B2M. The contribution of H2O to the spectrum of CRL 618 at 58 μm is negligible (Herpin & Cernicharo 2000).

3. DISCUSSION

The fact that the 58 μm feature is detected in all the selected C-rich post–asymptotic giant branch (AGB) objects clearly points toward a carbon-rich molecule as the carrier of the band. Several molecules with four atoms have low-frequency bending modes around 160–220 cm−1. HC3N, which has a low-energy bending mode, ν1, at 222.413 cm−1 (~45 μm). Dyacetylene, C2H2, recently detected in CRL 618 with a very large abundance (see Cernicharo et al. 2001a, 2001b), has a low-energy bending mode, ν2, also at ~45 μm. Another example of a molecule with bending modes in this wavelength range is C2H. Pure rotational lines from the ν1 = 1, 2 bending states of C2H have been detected in IRC +10216 by Güelin et al. (1987) and Yamamoto et al. (1987). The frequency of this mode is expected from ab initio calculations (Graf, Geiss, & Leutwyler 2001) to be around 178 cm−1.

Yamamoto et al. (1987) have estimated a frequency of 131 cm−1. This value agrees well with the series of peaks observed in the photoelectron spectroscopy of Arnold et al. (1991). The difference between the frequency of the new infrared band and that derived from the matrix experiments is 2.6 cm−1, which could be consistent with a frequency shift introduced by the Ar matrix of 1.5%. Ab initio calculations predict wave-numbers in the 175–214 cm−1 range (47–57 μm) and an infrared intensity of 46.2 km mol−1 [A(ν1 = 1–0) = 2.5 s−1]. Martin, François, & Gijbels 1991; Watts et al. 1992; Taylor & Martin 1996; see also Van Orden & Saykally 1998. Owing to the complexity of the C2H electronic energy levels and to the limited accuracy level of ab initio calculations, this intensity value has to be taken into account as a crude estimation.

The fact that the observed band (see Fig. 1) contains several spectral features suggests a transition between terms of higher spin multiplicity, in particular toward a vibronic transition 3Π–Σ or 3Π–Σ, i.e., just the type of bands we can expect for C3H and C4H, which have 3Σ and 3Π ground electronic states, respectively. The lowest bending modes of these species, ν1 for C3H and ν2 for C4H, will have 3Π and 3Π vibronic character, respectively. An argument against C3H is the following: while pure rotational lines of its bending mode have been detected toward IRC +10216 (Güelin et al. 1987; Yamamoto et al. 1987), these lines are missing in all other objects reported here (except in CRL 618, where several weak lines from these states have been detected; J. Cernicharo et al. 2003, in preparation). Moreover, the abundance of C3H in Sgr B2 is rather low (Güelin, Mezaoui, & Frielg 1982), while C4H has a large abundance (Cernicharo et al. 2000). Hence, it is tempting to assume that the observed features in post-AGB stars and in the ISM correspond to the ν1 mode of C3H, although a definitive assignment will require better spectral resolution data and/or additional laboratory information on this species. The main problem in assigning the band to the ν1 mode of C3H is the large spin–orbit interaction constant, ASO , that should have the 3Π vibronic state in order to reproduce the observations. As the ground electronic state of C3H is aΣ, a very small value for ASO should be expected. However, if the molecule has a low-lying excited electronic state with Λ ≠ 0, then the ground and the excited states will be strongly coupled through vibronic mixing and a large spin-orbit constant could be expected. This is the case for CCH, which has a Σ ground state and an Λ=2Π state 3600 cm−1 above. The ν1 bending mode of the ground electronic state has ASO = 0.3 cm−1. For C3H, ASO is very large, ~3 cm−1 (Yamamoto et al. 1987), because its Λ=2Π state is only ~468 cm−1 above the Σ ground state (see above). For C3H, the situation could be very similar to that of C2H, as its first excited electronic state is ^3Δ and is only 2680 cm−1 above the ground electronic Σ state (Arnold et al. 1991; Xu et al. 1997). The bottom panel in Figure 1 shows the computed band shape for ASO = 4 cm−1 at different temperatures. The similarity between the observed and computed shape is appealing. Nevertheless, we note that the adopted spin-orbit constant is particularly large. We have run several models with different ASO values and conclude that the shape of the band is...
Another possibility that may explain the complexity of the band shape and allows smaller $\alpha_{00}$ values is that $^{13}$C$_{3}$C and $^{13}$C$^{13}$C isotopomers also make a remarkable contribution to the observed emission. This could also apply to C$_{4}$H if finally this molecule is confirmed as the carrier. We note, however, that in this case we should also expect a very large column density of C$_{4}$H, which looks incompatible with the upper limits found for this molecule in Sgr B2 (Guélin et al. 1982). If the carrier is C$_{4}$, then the column density will be particularly large in all observed sources. Assuming a vibrational excitation temperature of 50–100 K in AGB stars and PPNs, $N$(C$_{4}$) has to be close to $10^{15}$ cm$^{-2}$, i.e., a typical abundance of a few times $10^{-7}$ to $10^{-6}$. In Sgr B2, the computed column density (assuming a lower vibrational excitation temperature) is $10^{12}$ cm$^{-2}$, i.e., similar to that derived by Cernicharo et al. (2000) for C$_{3}$. The accuracy of the band intensity from ab initio calculations dominates the error in the estimated column densities.

Future space-borne platforms, such as the Herschel Space Observatory, will be equipped with heterodyne instruments with much better spectral resolution, which should permit the detection of longer C$_{n}$ chains through their low-lying bending modes in the far-infrared. The detection of these molecules and the determination of their abundances will allow us to establish their role in the formation of the carriers of the unidentified infrared bands. While we wait for Herschel, important work has to be done in spectroscopy laboratories to fully characterize these molecular species.

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