Discovery of Interstellar Isocyanogen (CNCN): Further Evidence that Dicyanopolynes Are Abundant in Space*

M. Agúndez , N. Marcelino, and J. Cernicharo

Instituto de Física Fundamental, CSIC, C/ Serrano 123, E-28006 Madrid, Spain; marcelino.agundez@csic.es

Received 2018 June 4; revised 2018 June 22; accepted 2018 June 26; published 2018 July 13

Abstract

It is thought that dicyanopolynes could potentially be abundant interstellar molecules; though, their lack of a dipole moment makes it impossible to detect them through radioastronomical techniques. Recently, the simplest member of this chemical family, cyanogen (NCCN), was indirectly probed for the first time in interstellar space through the detection of its protonated form toward the dense clouds L483 and TMC-1. Here we present a second set of firm evidence indicating the presence of NCCN in interstellar space, namely the detection of the metastable and polar isomer isocyanogen (CNCN). This species has been identified in L483 and tentatively in TMC-1 by observing various rotational transitions in the λ 3 mm band with the IRAM 30 m telescope. We derive beam-averaged column densities for CNCN of $1.6 \times 10^{12} \text{ cm}^{-2}$ in L483 and $9 \times 10^{11} \text{ cm}^{-2}$ in TMC-1, which imply fractional abundances relative to H_2 in the range of $(5\text{--}9) \times 10^{-11}$. While the presence of NCCN in interstellar clouds seems undoubtable due to the detection of NCCNH^+ and CNCN, putting tight constraints on its abundance is still hampered by the poor knowledge of the chemistry that links NCCN with NCCNH^+ and especially with CNCN. We estimate that NCCN could be fairly abundant, in the range of $10^{-9}\text{--}10^{-7}$ relative to H_2 , such as other abundant nitriles like HCN and HC_3N .

Key words: astrochemistry – ISM: clouds – ISM: molecules – line: identification – radio lines: ISM

Supporting material: data behind figures

1. Introduction

Interstellar chemistry is essentially organic in nature. Around three-fourths of the nearly 200 molecules detected to date in interstellar and circumstellar media contain at least one carbon atom. Among them, there are alcohols, aldehydes, acids, ethers, and amines; however, the most prevalent functional group is that of nitriles (e.g., Agúndez & Wakelam 2013). Indeed, the strong bond of the cyano group $\text{C}\equiv\text{N}$ is present in more than 30 interstellar molecules, though until recently, no molecule containing two cyano groups had been observed in interstellar space (Agúndez et al. 2015a).

A particular subclass of molecules with two cyano groups are dicyanopolynes, which consist of a highly unsaturated linear skeleton of carbon atoms ended by a cyano group at each edge, i.e., $\text{N}\equiv\text{C}-(\text{C}\equiv\text{C})_n-\text{C}\equiv\text{N}$. These molecules are very stable and it has been suggested that they could be abundant in interstellar and circumstellar clouds (Kołos & Grabowski 2000; Petrie et al. 2003). The simplest member of this type of molecules, cyanogen (NCCN), is hypothesized to be a precursor of the widely observed cometary CN (Fray et al. 2005) and it has been identified in the atmosphere of Titan (Kunde et al. 1981), where the larger homologue NC_4N has been long thought to be present as well (Jolly et al. 2015). A chemical cousin of cyanogen in which one N atom is substituted by a P atom, NCCP, has been tentatively identified in the carbon-rich envelope IRC+10216 (Agúndez et al. 2014).

It is therefore reasonable to think that dicyanopolynes can be abundant in molecular clouds. However, their detection is hampered by the fact that they are nonpolar and therefore cannot be observed through their rotational spectrum. To

investigate the plausibility of this hypothesis, it was proposed that the presence of NCCN in interstellar and circumstellar clouds can be indirectly probed through the observation of chemically related polar molecules, such as protonated cyanogen (NCCNH^+) or the metastable isomer CNCN (Petrie et al. 2003). A few years ago, we succeeded in detecting protonated cyanogen in the cold dark clouds L483 and TMC-1 (Agúndez et al. 2015a). From the observed abundances of NCCNH^+ it was inferred that indeed NCCN should be as abundant as the nitriles HCN and HC_3N . In this Letter, we present the identification of isocyanogen (CNCN), a metastable isomer of NCCN, in L483 and a tentative detection toward TMC-1. This result brings further support to the hypothesis that dicyanopolynes are abundant molecules in interstellar space.

2. Observations

The observations of L483 were carried out with the IRAM 30 m telescope in the course of a λ 3 mm molecular line survey. Details of these observations are given in Agúndez et al. (2018) and Marcelino et al. (2018), while a thorough description of the complete survey will be presented elsewhere (M. Agúndez et al. 2018, in preparation). Briefly, observations were performed in several sessions from 2016 August to 2018 April, with the telescope pointed toward the position of the infrared source IRAS 18148–0440. We used the frequency-switching technique, with the receiver EMIR E090 connected to the FTS backend with a spectral resolution of 50 kHz.

The observations of TMC-1 were also taken with the IRAM 30 m telescope as part of a λ 3 mm spectral scan at the position of the cyanopolyne peak (Marcelino et al. 2005, 2007, 2009). A large fraction of the data was observed in 2012 February (see details in Cernicharo et al. 2012).

* Based on observations carried out with the IRAM 30 m Telescope. IRAM is supported by INSU/CNRS (France), MPG (Germany), and IGN (Spain).

Figure 1. Lines of CNCN observed toward L483 with the IRAM 30 m telescope. Lines are detected at $8-14\sigma$ confidence levels. The $J = 11 - 10$ line at 113.8 GHz is not detected due to the more limited sensitivity of the data at these frequencies. The data used to create this figure are available.

3. Results

The analysis of the λ 3 mm IRAM 30 m data of L483 has already resulted in the detection of several new interstellar molecules: HCCO (Agúndez et al. 2015b), NCCNH⁺ (Agúndez et al. 2015a), NS⁺ (Cernicharo et al. 2018), HCS, and HSC (Agúndez et al. 2018), as well as NCO and the confirmation of H₂NCO⁺ (Marcelino et al. 2018). A complete analysis of the λ 3 mm molecular line survey will be presented in a separate article (M. Agúndez et al. 2018, in preparation). Here we focus on three emission lines that can be unambiguously assigned to the $J = 8 - 7$, $J = 9 - 8$, and $J = 10 - 9$ rotational transitions of CNCN, lying at 82.8 GHz, 93.1 GHz, and 103.5 GHz (see Figure 1 and Table 1).

Isocyanogen (CNCN), a metastable isomer lying 1.06 eV above cyanogen (NCCN), is a linear molecule with a $^1\Sigma^+$ electronic ground state (Botschwina & Sebald 1990; Ding et al. 2000; Chaudhuri et al. 2006). Its rotational spectrum has been extensively characterized in the laboratory from 70 to 340 GHz (Winnewisser et al. 1992). The hyperfine structure due to the quadrupole of the two ^{14}N nuclei has been measured for the $J = 1 - 0$ and $J = 2 - 1$ lines, where the various components are separated by a few MHz (Gerry et al. 1990). However, the higher- J lines observed here have very small line

Figure 2. IRAM 30 m spectrum obtained toward TMC-1 by stacking four lines, the $J = 8 - 7$ through $J = 11 - 10$, of CNCN. The line is detected at a $5-6\sigma$ confidence level. The data used to create this figure are available.

Table 1
Observed Line Parameters of CNCN in L483

Transition	Frequency (MHz)	V_{LSR} (km s ⁻¹)	Δv (km s ⁻¹)	$\int T_A^* dv$ (K km s ⁻¹)
$J = 8 - 7$	82784.692	+5.21(7)	0.87(14)	0.0087(13)
$J = 9 - 8$	93132.326	+5.30(4)	0.47(14)	0.0052(4)
$J = 10 - 9$	103479.802	+5.37(3)	0.47(6)	0.0061(6)

Note. Numbers in parentheses are 1σ uncertainties in units of the last digits obtained from Gaussian fits.

splittings and cannot be spectrally resolved (see JPL catalog¹; Pickett et al. 1998). Isocyanogen is a moderately polar molecule, with a measured permanent electric dipole moment of 0.7074 ± 0.0052 D (Gerry et al. 1990). The species is included in the MADEx code² (Cernicharo 2012).

The spectra of L483 at 82.8 and 93.1 GHz have T_A^* rms noise levels of 2.2–2.3 mK per 50 kHz channel, which translates to detection confidence levels of $8-9\sigma$ for the $J = 8 - 7$ and $J = 9 - 8$ lines of CNCN. We note that the Gaussian fit to the $J = 8 - 7$ line results in a too large line width (0.87 km s^{-1} versus the value of 0.47 km s^{-1} obtained for the two other lines; see Table 1) which is probably a consequence of the presence of positive channels around the line which are within the noise but are taken as part of the line by the fitting algorithm. The spectrum at 103.5 GHz is more sensitive, with a T_A^* rms of 1.6 mK per 50 kHz channel, and the $J = 10 - 9$ line is detected at a higher confidence level of 14σ . This spectrum also clearly shows a weak line arising from methyl formate (see Figure 1). The line survey indeed shows many more lines of this complex organic molecule, which has recently been detected in L483 using ALMA (Oya et al. 2017). There is another rotational transition of CNCN, the $J = 11 - 10$ lying at 113.8 GHz, which falls within the frequency range covered by our line survey; though, in this spectral region the data is less sensitive (the T_A^* rms noise level is ~ 5 mK per 50 kHz channel) and the line is not clearly detected. With three lines well detected, we consider that the identification of CNCN in L483 is completely secure.

¹ <https://spec.jpl.nasa.gov/>

² https://nanocosmos.iff.csic.es/?page_id=1619

We have also searched for CNCN in our λ 3 mm data of TMC-1 obtained with the IRAM 30 m telescope. The data covers the four rotational transitions, $J = 8 - 7$ through $J = 11 - 10$. None of them are detected at a sufficient confidence level, but after stacking the spectra around the four lines, an emission line with a peak intensity of $T_A^* \sim 7$ mK appears centered at V_{LSR} of 5.85 ± 0.05 km s $^{-1}$, in agreement with the systemic velocity of TMC-1 measured in other molecular lines (e.g., Agúndez et al. 2015a). The line is detected at a $5-6\sigma$ confidence level. However, taking into account that it comes from a line stacking of four lines, we consider the detection to be tentative. More sensitive observations are needed to detect the individual lines with a sufficient signal-to-noise ratio.

From the intensities of the three CNCN lines detected in L483 and assuming a rotational temperature of 10 K, which is the gas kinetic temperature in this dense core as derived from NH $_3$ (Anglada et al. 1997), we find a beam-averaged column density for CNCN of 1.6×10^{12} cm $^{-2}$. In TMC-1, we estimate $N(\text{CNCN}) = 9 \times 10^{11}$ cm $^{-2}$, assuming a rotational temperature of 10 K (Pratap et al. 1997). Adopting H $_2$ column densities of 3×10^{22} cm $^{-2}$ for L483 (Tafalla et al. 2000) and 1×10^{22} cm $^{-2}$ for TMC-1 (Cernicharo & Guélin 1987), the abundance of CNCN relative to H $_2$ is then 5×10^{-11} in L483 and 9×10^{-11} in TMC-1. The metastable isomer CNCN is therefore significantly more abundant than protonated cyanogen, with column density ratios CNCN/NCCNH $^+$ of 40 and 10 in L483 and TMC-1, respectively.

The dense cores TMC-1 and L483 are rich in carbon chain molecules (e.g., Kawaguchi et al. 1995; M. Agúndez et al. 2018, in preparation), and this common feature may be at the origin of the presence of cyanogen in both clouds. The two sources are, however, different in that TMC-1 is a starless core that displays narrow lines (Soma et al. 2018), while L483 hosts a Class 0 protostar and some molecules show wide lines for which part of the emission arises from an outflow (e.g., H $_2$ CO; Tafalla et al. 2000) or from a compact hot corino around the protostar, as revealed by recent ALMA observations (e.g., HNCO; Oya et al. 2017). The narrow line profiles of CNCN in L483 point to emission from the ambient cloud. We estimate a 3σ upper limit to the abundance of CNCN in the hot corino of $(5-7) \times 10^{-9}$ relative to H $_2$, adopting a source diameter of $0''.5$, a line width of 10 km s $^{-1}$, a rotational temperature of 70–130 K, and $N(\text{H}_2) = 6.5 \times 10^{23}$ cm $^{-2}$ (see Oya et al. 2017).

4. Discussion

The discovery of CNCN opens a new venue, in addition to that provided by NCCNH $^+$, to probe the presence of the stable and likely abundant, though nonpolar, cyanogen molecule (NCCN). However, in order to use these species as markers of cyanogen it is necessary to understand the underlying chemical relationships between them.

The chemistry of NCCNH $^+$ and its chemical connection with NCCN was studied by Petrie et al. (2003) and more recently by Agúndez et al. (2015a). In both studies, the NCCNH $^+$ /NCCN abundance ratio predicted from a cold dark cloud chemical model is of the order of 10^{-4} . Therefore, the observed abundances of NCCNH $^+$ put the abundance of NCCN in dark clouds at the level of $(1-10) \times 10^{-8}$ relative to H $_2$ (Agúndez et al. 2015a). We note, however, that in this latter study the observed abundance ratios between the protonated and nonprotonated forms of the related cyanides HCN (and

HNC) and HC $_3$ N are underestimated by the chemical model by roughly a factor of 10. If the same holds for NCCN, its abundance would need to be revised downward to $(1-10) \times 10^{-9}$ relative to H $_2$.

In the case of the isomer CNCN, little is known about its chemistry and thus it is difficult to relate the observed abundance to that of NCCN. However, as noted by Petrie et al. (2003), this pair of isomers share structural characteristics (namely, a $-\text{CNC}$ versus a $-\text{CCN}$ subunit) with HCCNC and HCCCN, both of which are observed in cold dark clouds. Concretely, in L483 and TMC-1 the HCCNC/HCCCN column density ratio is around 50 (details for L483 will follow in M. Agúndez et al. 2018, in preparation; see, e.g., Agúndez & Wakelam 2013 for TMC-1). If the CNCN/NCCN abundance ratio is similar, the observed abundances of CNCN in L483 and TMC-1 would imply an NCCN abundance of $(2.5-4.5) \times 10^{-9}$ relative to H $_2$. It is worth noting that these values are in the range of abundances inferred above from NCCNH $^+$ adopting an NCCNH $^+$ /NCCN abundance ratio of 10^{-3} , instead of 10^{-4} .

In any case, it is clear that a better understanding of the chemistry of NCCN, CNCN, and NCCNH $^+$ in interstellar clouds is necessary to draw more robust conclusions. It is therefore worth revisiting what is known and in which directions further research is needed.

It is well established that the reaction between CN and HCN, which is exothermic to yield cyanogen, has an important activation barrier that makes it too slow at low temperatures (Yang et al. 1992). Therefore, the most plausible formation route of NCCN in cold clouds is the reaction

which involves two abundant reactants and is barrierless to produce NCCN, though, not when forming CNCN (Petrie et al. 2003). It would nevertheless be interesting to revisit this reaction through experiments or dynamical calculations to quantify the kinetics of the various possible channels. It is difficult to envisage other feasible (rapid and involving abundant reactants) NCCN-forming reactions. Another possible route is the reaction between N and HCCN, for which Loison et al. (2015) estimate a moderate rate coefficient of a few times 10^{-11} cm 3 s $^{-1}$; though, this reaction would be less efficient than reaction 1(a) owing to the low abundance of HCCN. Reactions of N $_2$ with radicals are unlikely to be exothermic due to the strong triple bond of molecular nitrogen. For example, the reaction between N $_2$ and C $_2$ H to produce NCCN is endothermic by ~ 50 kJ mol $^{-1}$.

If neutral–neutral gas-phase routes are not efficient enough, routes involving ions may do the work. The most obvious is

which could reasonably lead to NCCN + H or CNCN + H, although neither the rate coefficient nor the product distribution have been measured. A similar mechanism involving the ion HCNH $^+$ is thought to form HCN and HNC in dark clouds (e.g., Agúndez & Wakelam 2013). Note that if NCCNH $^+$ is the precursor of NCCN, and not the reverse, as occurs if NCCN is mainly formed by neutral–neutral routes like reaction 1(a), then the NCCNH $^+$ /NCCN abundance ratio will no longer be of the

order of 10^{-4} , but significantly higher. The question then would be how can NCCNH^+ be efficiently formed, typically from smaller fragments. One possible candidate is

which is a potentially important source of NCCNH^+ because the reactants are relatively abundant. Reaction (3) is nearly thermoneutral and thus it is unclear whether or not it is rapid at low temperatures. The reaction between HCNH^+ and HCN is exothermic in the channel yielding NCCNH^+ . However, the main channel appears to be $\text{HCNH}^+ + \text{CN}$ (Huntress et al. 1969) and besides, the reactant HCNH^+ should not be very abundant in dark clouds. Other potentially interesting reactions forming NCCNH^+ are $\text{C}_2\text{N}^+ + \text{NH}_2$ and $\text{C}_2\text{NH}^+ + \text{NH}$; though, the reactants are probably not abundant enough in dark clouds. The isomer CNCN can be formed in the dissociative recombination of NCCNH^+ with electrons if some important rearrangement takes place. A study of the product distribution of reaction (2) would allow us to validate or refute this possibility. If NCCNH^+ is not a viable precursor for CNCN , then protonated isocyanogen (either HCNCN^+ or CNCNH^+ , both having similar energies; Petrie 1998; Ding et al. 2001) could be the main precursor. However, protonated isocyanogen is $60\text{--}65 \text{ kJ mol}^{-1}$ less stable than protonated cyanogen (Petrie 1998) and thus forming it would be more difficult. For example, while a priori reaction (3) is a viable route to NCCNH^+ , the channel leading to HCNCN^+ or CNCNH^+ is probably endothermic.

A synthetic route to NCCN and CNCN alternative to the gas phase could take place on dust grains by recombination of two CN radicals. It is, however, uncertain whether the abundance of CN on grain surfaces is high enough. The CN radical, as other nitrogen-bearing species, tend to show little depletion from the gas phase in dense cores (Hily-Blant et al. 2008). It is also not clear whether such a reaction may have some barrier and ultimately how effective the desorption of these species would be for the gas phase.

Whatever the mechanism of formation of NCCN , it is likely to have a long life time in cold dark clouds because it is not a very reactive species, although the same may not be true for CNCN . Cyanogen shows a moderate reactivity with ions (McEwan & Anicich 1995) and it does not react at low temperature with H or O atoms (see NIST database³). However, it reacts with C and N atoms

with rate coefficients of a few times $10^{-11} \text{ cm}^3 \text{ s}^{-1}$ at room temperature (Safrany & Jaster 1968; Whyte & Phillips 1983). However, taking into account that reactions (4) and (5) are thought to be the main depletion mechanisms of NCCN (Agúndez et al. 2015a), it would be interesting to study their low-temperature kinetics.

5. Prospects

There are various directions to advance in our understanding of the presence and abundance of cyanogen and dicyanopolynes

Figure 3. Main formation (neutral in green and ionic in blue) and destruction (in red) pathways for NCCN and CNCN . The low-temperature kinetics of these reactions is very poorly constrained.

in interstellar space. The first one would be to study reactions (1)–(5) either experimentally or theoretically (see Figure 3) to better understand the chemical relationship of NCCNH^+ and CNCN with the likely abundant but unobservable NCCN .

The astronomical search for other markers of cyanogen is also an interesting possibility. For example, apart from CNCN , there are another two linear metastable isomers of NCCN . These are di-isocyanogen (CNNC) and diaza-dicarbon (NNCC), isomeric forms that lie higher in energy, specifically at 3.16 and 3.90 eV, respectively, above NCCN (Ding et al. 2000; Chaudhuri et al. 2006). While CNNC is nonpolar, NNCC is calculated to have a large dipole moment of 3.35 D (Ding et al. 2000), and it is thus a candidate for interstellar detection. This isomer, however, seems elusive to laboratory detection (Maier et al. 1992) and therefore its rotational spectrum remains unknown. An astronomical search for the protonated form of CNCN , either HCNCN^+ or CNCNH^+ (Petrie 1998; Ding et al. 2001), would also provide valuable information on the chemical origin of CNCN , but the rotational spectrum has not been measured.

If cyanogen is really an abundant species in interstellar clouds, it is conceivable that larger members of the series of dicyanopolynes are present as well. The next member is dicyanoacetylene (NC_4N), which, as NCCN , is nonpolar and thus indirect strategies to probe it are necessary. Dicyanoacetylene can be efficiently formed through the reactions $\text{CN} + \text{HC}_3\text{N}$ or $\text{C}_3\text{N} + \text{HCN/HNC}$, which are barrierless according to calculations by Petrie & Osamura (2004). An astronomical search for the protonated form of NC_4N is not yet feasible because there is little spectroscopic information on this ion. However, the metastable isomer NC_3NC , which lies 1.12 eV above NC_4N has a moderate calculated dipole moment of 1.04–1.096 D (Horn et al. 1994; Lee 1998), and its rotational spectrum has been measured in the laboratory (Huckauf et al. 1999). It is not present in our $\lambda 3 \text{ mm}$ data of L483 and TMC-1; though, this is probably not the best wavelength range to search for such a heavy molecule in cold sources. A search at longer wavelengths may prove more fruitful. There are another two metastable isomers, but one (CNC_2NC) is nonpolar while for the other (NCNC_3), which lies 2.60 eV above NC_4N (Jiang et al. 2004), spectroscopic data is lacking.

³ <https://kinetics.nist.gov/kinetics/>

A better understanding of the chemistry of NCCN in interstellar space would benefit from the search for the already detected species NCCNH^+ and CNCN in other sources, ranging from prestellar cores to star-forming regions. Getting access to the spatial distribution of these species in the targeted clouds will also help; though, lines are weak and obtaining emission maps will be difficult, especially if NCCN and their markers NCCNH^+ and CNCN have an extended distribution over the ambient cloud, which is the most likely possibility. Finally, a direct search for NCCN at infrared wavelengths with telescopes like SOFIA or *JWST* may prove to be fruitful for strong infrared sources.

6. Conclusions

We have reported on the first identification in space of isocyanogen (CNCN), a metastable isomer of cyanogen. This species has been observed in the dense core L483 and tentatively in TMC-1, where we previously reported the detection of protonated cyanogen (NCCNH^+). We derive fractional abundances of several times 10^{-11} relative to H_2 for CNCN . The detection of CNCN together with that of NCCNH^+ in dark clouds supports the idea that NCCN and larger dicyanopolynes, all of which are nonpolar and thus cannot be directly observed through their rotational spectrum, are abundant in molecular clouds. We estimate that the abundance of NCCN may be in the range of 10^{-9} – 10^{-7} relative to H_2 . A better knowledge of the chemistry of NCCN and dicyanopolynes in space will benefit from experimental and/or theoretical studies of some key reactions together with sensitive astronomical observations of NCCNH^+ , CNCN , and related species not yet identified in space.

We thank the IRAM 30m staff for their help during the observations and the anonymous referee for useful comments. We acknowledge funding support from the European Research Council (ERC Grant 610256: NANOCOSMOS) and from Spanish MINECO through grant AYA2016-75066-C2-1-P. M.A. also acknowledges funding support from the Ramón y Cajal programme of Spanish MINECO (RyC-2014-16277).

ORCID iDs

M. Agúndez <https://orcid.org/0000-0003-3248-3564>

J. Cernicharo <https://orcid.org/0000-0002-3518-2524>

References

- Agúndez, M., Cernicharo, J., de Vicente, P., et al. 2015a, *A&A*, **579**, L10
 Agúndez, M., Cernicharo, J., & Guélin, M. 2014, *A&A*, **570**, A45
 Agúndez, M., Cernicharo, J., & Guélin, M. 2015b, *A&A*, **577**, L5
 Agúndez, M., Marcelino, N., Cernicharo, J., & Tafalla, M. 2018, *A&A*, **611**, L1
 Agúndez, M., & Wakelam, V. 2013, *ChRv*, **113**, 8710
 Anglada, G., Sepúlveda, I., & Gómez, J. F. 1997, *A&AS*, **121**, 255
 Botschwina, P., & Sebald, P. 1990, *CP*, **141**, 311
 Cernicharo, J. 2012, in European Conference on Laboratory Astrophysics, EAS Publications Series, Vol. 58, ed. C. Stehl, C. Joblin, & L. d'Hendecourt (Cambridge: Cambridge Univ. Press), 251
 Cernicharo, J., & Guélin, M. 1987, *A&A*, **176**, 299
 Cernicharo, J., Lefloch, B., Agúndez, M., et al. 2018, *ApJL*, **853**, L22
 Cernicharo, J., Marcelino, N., Roueff, E., et al. 2012, *ApJL*, **759**, L43
 Chaudhuri, R. K., Krishnamachari, S. L. N. G., & Freed, K. F. 2006, *JMoSt*, **768**, 119
 Ding, Y.-H., Li, Z.-S., Huang, X.-R., & Sun, C.-C. 2000, *JChPh*, **113**, 1745
 Ding, Y.-H., Li, Z.-S., Huang, X.-R., & Sun, C.-C. 2001, *JPCA*, **105**, 7085
 Fray, N., Bénilan, Y., Cottin, H., Gazeau, M.-C., & Crovisier, J. 2005, *P&SS*, **53**, 1243
 Gerry, M. C. L., Stroh, F., & Winniewisser, M. 1990, *JMoSp*, **140**, 147
 Hily-Blant, P., Walmsley, M., Pineau Des Forêts, G., & Flower, D. 2008, *A&A*, **480**, L5
 Horn, M., Botschwina, P., & Flügge, J. 1994, *AcTC*, **88**, 1
 Huckauf, A., Guarnieri, A., Heyl, A., et al. 1999, *CPL*, **303**, 607
 Huntress, W. T., Jr., Baldeschwieler, J. D., & Ponnampuruma, C. 1969, *Natur*, **223**, 468
 Jiang, Z.-Y., Xu, X.-H., Wu, H.-S., et al. 2004, *IJC*, **97**, 876
 Jolly, A., Cottini, V., Fayt, A., et al. 2015, *Icar*, **248**, 340
 Kawaguchi, K., Kasai, Y., Ishikawa, S.-I., & Kaifu, N. 1995, *PASJ*, **47**, 853
 Kolos, R., & Grabowski, Z. R. 2000, *Ap&SS*, **271**, 65
 Kunde, V. G., Aikin, A. C., Hanel, R. A., et al. 1981, *Natur*, **292**, 686
 Lee, S. 1998, *JMoSt*, **427**, 267
 Loison, J. C., Hébrard, E., Dobrijevic, M., et al. 2015, *Icar*, **247**, 218
 Maier, G., Reisenauer, H. P., Eckwert, J., et al. 1992, *Angew. Chem. Int. Ed. Engl.*, **31**, 1218
 Marcelino, N., Agúndez, M., Cernicharo, J., et al. 2018, *A&A*, **612**, L10
 Marcelino, N., Cernicharo, J., Agúndez, M., et al. 2007, *ApJL*, **665**, L127
 Marcelino, N., Cernicharo, J., Roueff, E., et al. 2005, *ApJ*, **620**, 308
 Marcelino, N., Cernicharo, J., Tercero, B., & Roueff, E. 2009, *ApJL*, **690**, L27
 McEwan, M. J., & Anicich, V. G. 1995, *JPhCh*, **99**, 12204
 Oya, Y., Sakai, N., Watanabe, Y., et al. 2017, *ApJ*, **837**, 174
 Petrie, S. 1998, *JPCA*, **102**, 7835
 Petrie, S., Millar, T. J., & Markwick, A. J. 2003, *MNRAS*, **341**, 609
 Petrie, S., & Osamura, Y. 2004, *JPCA*, **108**, 3623
 Pickett, H. M., Poynter, R. L., Cohen, E. A., et al. 1998, *JQSRT*, **60**, 883
 Pratap, P., Dickens, J. E., Snell, R. L., et al. 1997, *ApJ*, **486**, 862
 Safrany, D. R., & Jaster, W. 1968, *JPhCh*, **72**, 3305
 Soma, T., Sakai, N., Watanabe, Y., & Yamamoto, S. 2018, *ApJ*, **854**, 116
 Tafalla, M., Myers, P. C., Mardones, D., & Bachiller, R. 2000, *A&A*, **359**, 967
 Whyte, A. R., & Phillips, L. F. 1983, *CPL*, **98**, 590
 Winniewisser, M., Seibert, J. W. G., & Yamada, K. M. T. 1992, *JMoSp*, **153**, 635
 Yang, D. L., Yu, T., Lin, M. C., & Melius, C. F. 1992, *JChPh*, **97**, 222