On C3 molecules in diffuse interstellar clouds

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On C_3 molecules in diffuse interstellar clouds

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Summary. A search for absorption lines of interstellar C_3 has been made. The $\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma_g^+$ band near 4050 Å was not detected. Upper limits on the C_3 column density are $f = N(C_3)/N(H + H_2) \lesssim 1 \times 10^{-9}$ for several diffuse interstellar clouds and $f < 3 \times 10^{-9}$ for the cool core of the ζ Oph cloud. Useful laboratory studies for this molecule are pinpointed.

1 Introduction

The physical conditions and chemical composition of diffuse interstellar clouds are deduced from studies of atomic and molecular absorption lines in the spectra of reddened hot stars. Snow (1980) offers a compilation of molecules detected in this way. The diffuse clouds are generally characterized by low gas densities, $n \sim 10$–$500\,cm^{-3}$ and small extinction values, $A_V < 3$ mag. However, Black & Dalgarno (1977, hereafter BD) proposed a model for the cloud towards ζ Oph which includes a cool denser core having a kinetic temperature of 22 K and a total density $n = 2500\,cm^{-3}$. Molecules such as H_2, CO and C_2 are predicted to be concentrated in such cloud cores, where the attenuation of interstellar ultraviolet radiation favours molecular formation. C_2, a recent addition to the list of interstellar molecules, has been observed towards VI Cygni No. 12 (Souza & Lutz 1977), ζ Oph (Chaffee & Lutz 1978) and ζ Per (Chaffee *et al.* 1980). In view of the interest in linear carbon chain molecules seen in molecular clouds, we report here a search for C_3.

The C_3 molecule is already of considerable interest in astrophysics: an electronic transition from the ground state, $\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma_g^+$, is observed at 4050 Å in comets (Swings 1942), cool carbon stars (Swings, McKellar & Rao 1953), and in an F supergiant circumstellar shell (Crampton, Cowley & Humphreys 1975). This linear symmetric molecule is very stable, with a dissociation energy to atoms of 13.6 eV and to $C_2 + C$ of 7.5 eV (JANAF 1971). Douglas (1977) suggested that the diffuse interstellar bands might be ascribed to long-chain carbon molecules C_n with $n > 5$, shorter chains being photodissociated or ionized. Detection of C_3 could add weight to this suggestion. Mitchell, Ginsburg & Kurtz (1979)

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described a chemical model for diffuse clouds in which the C_2 and C_3 concentrations were found to be sensitive functions of gas density. Their predicted column density for the BD model of the ζ Oph cloud, $N(C_3) > 10^{13}$ cm^{-2}, together with a favourable oscillator strength $f_{el} = 0.025$ (Becker, Tatarczyk & Radić-Perić 1979), corresponds to an easily detectable absorption feature (equivalent width $W_\lambda > 20$ mÅ).

The purpose of this paper is to present new observations at 4050 Å of reddened stars, to give an analysis of the excitation of C_3 levels and to discuss limits on the C_3 abundance. Herbig (1968) reported, without comment, an upper limit for a C_3 absorption feature towards ζ Oph: $W_\lambda < 2$ mÅ. However, it is not clear how this should be interpreted because a broad, unresolved band is expected (as discussed in Section 3). We also report new calculations of the C_3 concentration as a function of gas density and A_V, intended as a guide in selecting clouds which might have detectable C_3.

2 Observations

Spectra of reddened early-type stars were obtained at the McDonald Observatory 2.7-m telescope with the coudé spectrograph equipped with either a Reticon (Vogt, Tull & Kelton 1978) or Digicon detector (Tull, Choisser & Snow 1975). Details of the stars observed and the spectra obtained are listed in Table 1. Three gratings were used, one blazed at 4000 Å in first order and providing a bandpass of 100 Å at a resolution of 0.2 Å, one blazed at 6000 Å (first order) but used in second order to achieve 0.1 Å resolution over a 50 Å bandpass and an echelle grating providing spectra with 0.05 Å resolution within a 17 Å bandpass. Here, resolution refers to the FWHM of hollow cathode Fe and Ne lines observed with the same instrumental set-up. For several of the bright stars, successive spectra were taken at slightly different grating settings and were later shifted and co-added. This was done to reduce a low-amplitude ripple in the instrumental response with a second contribution from the interference filter used with the echelle. A white-light source was used to correct for the diode-to-diode sensitivity variations; however, the illumination of the spectrograph by the star and the lamp differ slightly and a small residual ripple remains.

The stars selected were considered to be leading candidates for a C_3 detection. The C_3 abundance is predicted to increase steeply with increasing extinction (especially at $A_V \approx 1.5$ mag) and density. In several cases, measured column densities of H, H_2, CO and C_2 indicate the presence of a moderately dense diffuse cloud along the line-of-sight; the ratios $N(H_2)/N(H + 2H_2)$ and $N(CO)/N(H + 2H_2)$ were taken as density indicators. In particular, two-component cloud models include cool dense cores with $T = 22$ K and $n = 2500$ cm^{-3} for ζ Oph (BD) and $T = 45$ K, $N = 500$ cm^{-3} for ζ Per (Black, Dalgarno & Hartquist 1978). (Note that Crutcher & Watson 1981 have proposed a rather different model for the ζ Oph cloud, as

Table 1. The programme stars.

Name	HD	V (km s^{-1})	B (mag)	$E(B-V)$	Sp.	Resolution (Å)
ζ Oph	149757	−15 (1)	2.5	0.33	O9.5 V	0.05, 0.2
ζ Per	24398	+15 (2)	2.9	0.32	B1 IB	0.2
	23753	+14 (3)	5.3	0.02	B8 V	0.2
	183143	−2, +42 (3)	8.1	1.26	B1 Ia	0.2
55 Cyg	198478	−12 (1)	5.2	0.53	B3 Ia	0.1
26 Cep	213087		5.8	0.62	B0.5 Ib	0.1

References: (1) Hobbs (1974). (2) Chaffee *et al.* (1980). (Wilson (1953).

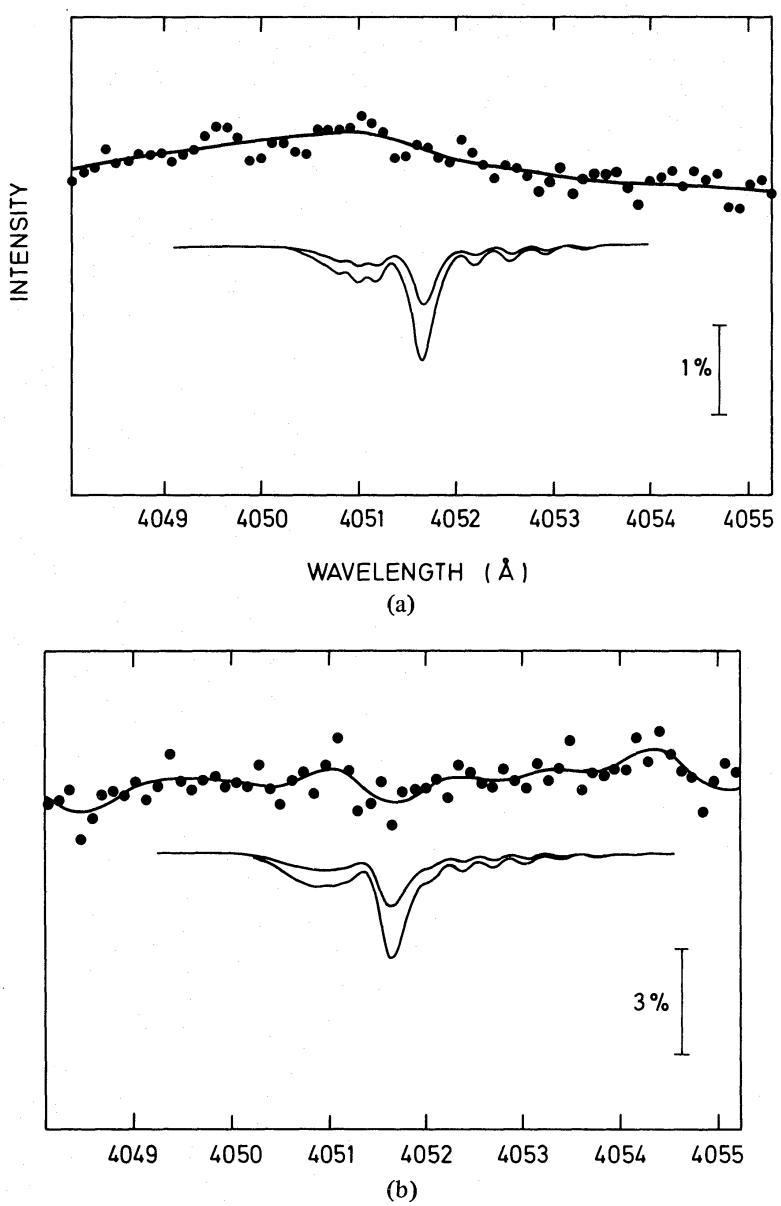

Figure 1. (a) Spectrum of ζ Oph near 4050 Å. Dots show individual channels in the observed spectrum (resolution 0.2 Å) which represents five co-added spectra. The synthetic spectra show the predicted C_3 spectrum for the case $T_{rot} = 22$ K, $N(C_3) = 1.5 \times 10^{12}$ cm^{-2} and 3.0×10^{12} cm^{-2}. (b) Spectrum of HD 183143 near 4050 Å. The dots indicate co-added Digicon spectra of resolution 0.2 Å. The synthetic spectra were calculated for $T_{rot} = 40$ K, $N(C_3) = 4.5 \times 10^{12}$ cm^{-2} and 9.0×10^{12} cm^{-2}.

discussed in Section 5 below.) Other stars were included on the basis of reddening alone; for example, HD 183143 which has $E(B-V) = 1.26$ and whose spectrum shows strong diffuse bands (Herbig 1975). The heliocentric velocities assumed for the interstellar lines are given in Table 1; if no measurement existed, the range $v = -100$ to $+100$ km s^{-1} was searched.

The upper limits for W_λ for the C_3 (0,0,0 – 0,0,0) band are also listed in Table 1. The procedure for setting the W_λ limit, which refers to the whole band (P, Q, and R branches) can be seen in Fig. 1, where portions of typical spectra around 4050 Å are compared with synthetic spectra. The curvature of the continuum in the ζ Oph spectrum is caused by the presence of rotationally-broadened stellar absorption lines to the red and blue of 4050 Å.

The absorption features include contributions from O II and N II to the blue, and from O II and possibly N IV to the red. The high rotation velocity of ζ Oph ($v \sin i = 396\,\mathrm{km\,s^{-1}}$, Uesugi & Fukuda 1970) ensures that there is no confusion between stellar and interstellar features for this star. In contrast, for ζ Per there was some confusion caused by weak stellar lines (FHWM = 0.9 Å) and our upper limit is higher than that expected for the signal-to-noise ratio of the spectrum (~ 500:1). It should be noted that the upper limits set depend somewhat on the assumed C_3 rotational temperature.

3 The C_3 column density

Upper limits to the column density of C_3 have been calculated from the weak-line approximation for the absorption band equivalent width:

$$W_\lambda = \frac{\pi e^2}{mc^2} N_0 f_{000} \lambda^2$$

where $f_{000} = q_{000} f_{el}$ is the band oscillator strength and N_0 the column density of absorbers in all rotational levels of the vibrational ground state. This state is conventionally denoted $(v_1, v_2, v_3) = (0, 0, 0)$ where the quantum numbers refer to the symmetric stretching, the bending and the asymmetric stretching vibrational modes respectively.

The radiative lifetime of several vibrational levels in the upper $^1\Pi_u$ state was measured through a laser fluorescence technique (Becker *et al.* 1979). The lifetime, $\tau = 200 \pm 10$ ns, gives an electronic absorption oscillator strength $f_{el} = 0.025 \pm 0.001$ and $f_{000} = 0.018 \pm 0.001$ for the Franck–Condon factor $q_{000} = 0.74$ (Becker *et al.* 1979). Cooper & Jones (1979) measured the absorption cross-section of C_3 produced behind a shock wave in a C_2H_2–Ar mixture. Their result $f_{el} = 0.033 \pm 0.008$ is consistent with the lifetime-based result. This uncertainty estimate does not include an additional ±40 per cent uncertainty afflicting the predicted C_3 densities. Two other experiments, which are discussed by Cooper & Jones, are compatible with these f_{el} estimates to within the large uncertainties (±40 per cent to a factor of 3).

There is currently a marked disagreement between the experimental lifetime and f_{el} value and *ab initio* predictions. Römelt, Peyerimhoff & Buenker (1978) predict $\tau = 102$ ns and $f_{el} = 0.049$ from a SCF + CI calculation; see, also, Perić-Radić et al. (1977), who predicted $f_{el} = 0.061$ using a smaller basis set. The theoretical f_{el} is about a factor of 2 larger than the lifetime based estimate. Clearly additional experimental and theoretical work is needed to resolve this discrepancy. We adopt the lifetime result. If the theoretical f_{el} value is later confirmed, our estimates of the C_3 column density will need to be revised downwards. Note that our calculations combine the value $f_{000} = 0.018$ with rotational line strengths $S_J(P) = (J-1)/2$, $S_J(Q) = (2J+1)/2$ and $S_J(R) = (J+2)/2$.

The conversion of N_0 to $N(C_3)$, the total column density of molecules, requires knowledge of rotational and vibrational level populations in the molecule. In the remainder of this section we show that the rotational temperature should equal the gas kinetic temperature, but that there will be no significant population in excited vibrational levels, so that $N_0 \equiv N(C_3)$.

Interstellar molecules with significant dipole moments, such as CH or CN, show absorption only from the lowest one or two rotational levels, because radiative de-excitation of the rotational levels by electric dipole transitions occurs more rapidly than collisional excitation of these levels. In contrast, a homonuclear molecule like C_2 has no dipole moment and, because collisions play an important role in the excitation and de-excitation, the rotational

levels are nearly thermalized, i.e. $T_{rot} \simeq T_K$, the gas kinetic temperature. In its ground electronic state, C_3 is a linear symmetric molecule (Gausset *et al.* 1965) and, therefore, cannot possess a dipole moment. Two possible departures from this linearity are briefly discussed. First, Carter, Mills & Murrell (1980) show that a quasi-stable bent configuration exists. Since the activation energy above the linear (0, 0, 0) state is 0.26 eV (equivalent to 3000 K), this excited state is most probably not involved in the statistical equilibrium of the linear (0, 0, 0) state. Secondly, in excited vibrational levels the wavefunction symmetries could permit the existence of a small dipole moment if interactions between bending vibrations in perpendicular planes resulted in an effective bending of the molecule. However, this effect cannot occur in the ground (0, 0, 0) vibrational state because of its Σ_g^+ vibronic character (the (0, 1, 0) state has Π_u vibronic symmetry). We show below that the population of C_3 molecules in excited vibrational states is negligible. For the (0, 0, 0) state, rotational levels with odd J do not exist and, hence, only quadrupole radiative transitions with $\Delta J = 2$ are possible. Even in diffuse clouds, radiative rates are then orders of magnitude slower than collisional rates with H or H_2 and thus $T_{rot} = T_K$. Cloud core temperatures are expected to be 20–50 K (BD; Black *et al.* 1978). We adopt $T_{rot} = 40$ K for clouds where no model exists.

Chaffee *et al.* (1980) suggested that the level populations of C_2 are affected by pumping via electronic transitions. Indeed, the observed rotational temperature for C_2 towards ζ Per, $T_{rot} = 97$ K, was higher than the expected gas kinetic temperature (45 K) and this difference was plausibly attributed to radiative pumping. A similar effect could occur in C_3, via an excited $^1\Sigma_u^+$ state which has been predicted by Römelt *et al.* (1978). The calculated excitation energy of this state is 8.03 eV and the predicted oscillator strength, $f_{el} = 0.92$ for $^1\Sigma_u^+ - X\,^1\Sigma_g^+$; the latter transition would occur near 1540 Å. Laboratory spectroscopy of C_3 only extends down to 1950 Å (Weltner & McLeod 1966) and no states above the $^1\Pi_u$ have been observed as yet. Detailed calculations of any C_3 ultraviolet pumping are not yet possible, but we note that this transition may play an important role because of its predicted strength. At low densities ($n \lesssim 50\,cm^{-3}$) radiative excitation of the rotational levels, via the 4050 Å band itself, could also lead to a departure of T_{rot} from T_{kin}. The upwards collisional and radiative rates are equal for a density $n_{tot} = 2\,cm^{-3}$ at $A_v = 1$ mag. Excitation via the 4050 Å band probably exceeds the rate via the 1540 Å band for $A_v \gtrsim 1.5$ mag. If $T_{rot}(C_3)$ were higher, the 4050 Å band would be broader and shallower and more difficult to detect. At $T = 100$ K the Q-branch central depth is only 40 per cent of its value for $T = 22$ K.

Vibrational excitation of C_3 must be considered because the bending vibrational frequency $\omega_2 = 63\,cm^{-1}$ is equivalent to only 90 K. The other vibrational modes have frequencies (ω_1 and ω_3) larger than $1200\,cm^{-1}$ and their excitation is neglected here. The vibrational partition function may be written as $[1 - \exp(-90/T_{vib})]^{-1}$. However, T_{vib} will not be much larger than 3 K, the background radiation temperature, because electric dipole allowed transitions occur between vibrational states with $\Delta v_2 = 1$, e.g. (0,1,0) – (0,0,0) within the ground electronic state. Although the (0, 0, 0) state with Σ^+ vibronic symmetry contains only even J levels, the (0, 1, 0) state with Π_u symmetry contains all J levels and, hence, vibrational transitions with $\Delta J = 0, \pm 1$ can occur.

The radiative de-excitation rate from $v_2 = 1$ can be estimated from the harmonic oscillator relation:

$$A(v + 1 \rightarrow v) = 5.3 \times 10^{-6}\,(v + 1)\,\frac{\omega_e^2}{\bar{\mu}}\left(\frac{d\mu}{dr}\right)^2\ s^{-1}$$

where $\bar{\mu}$ = reduced mass in amu, ω_e is the vibrational frequency in cm^{-1} and $d\mu/dr$ is the dipole moment derivative in Debye $Å^{-1}$. A Mulliken gross charge analysis (Clementi & Clementi 1962) indicates that the central C atom is positively charged by 0.79 e: $d\mu/dr$

would then be 3.8 D Å^{-1}. A conservative lower limit is surely $d\mu/dr = 0.01$ D Å^{-1} and thus, $A = 5 \times 10^{-7}$ s^{-1}.

The collisional de-excitation rate C_{ul}, typically 10^{-13} cm^3 s^{-1} for diatomic molecules with H_2 at 300 K, has only been measured for C_3 with C_3H_4 as the perturber: Lesiecki *et al.* (1980) found $C_{ul} = 5 \times 10^{-12}$ cm^3 s^{-1} for (0, 1, 0) → (0, 0, 0) at an unspecified (high) temperature. We assume that this rate applies to collisions with cold H_2 (the rate at $T = 22$ K is likely to be lower because C_{ul} is a sensitive function of temperature when $T_K < E_{vib}/k$, Millikan & White 1963).

Using these rates we calculate the relative populations having $v_2 = 0$ and 1. Absorption and stimulated emission are negligible and so, for the 2-level system ($v_2 = 0$ and 1)

$$n(010)/n(000) = \frac{n(H_2)C_{lu}}{A + n(H_2)C_{ul}} \simeq 1 \times 10^{-3}$$

for $T_K = 40$ K and $n(H_2) = 10^3$ cm^{-3}. The equivalent vibrational temperature is $T_{vib} = 13$ K. We note that the effective dipole moment derivative will probably be much larger than 0.01 D Å^{-1} and therefore the C_3 fraction with excited vibrational levels is even smaller than 10^{-3}.

Vibrational excitation could also occur via the $^1\Sigma_u^+ - X\,^1\Sigma_g^+$ bands or the 4050 Å bands. Inspection of the $A\,^1\Pi - X\,^1\Sigma_g^+$ Frank–Condon factors (Jungen & Merer 1980) suggests that 10–20 per cent of 4050 Å absorptions lead to vibrational excitation. However, the lowest excited level which could be directly populated is the $v_2 = 2$ level (181 K above the $v_2 = 0$ level), because transitions between even- and odd-numbered vibrational levels are forbidden within this electronic transition. Population of the $X\,^1\Sigma_g^+$ $v_2 = 2$ level is followed by a cascade to the ground level, either by allowed radiative transitions (with $\Delta v = 1$ or 2). We have investigated the 3-level system ($v_2 = 0$, 1, 2) in which 20 per cent of all 4050 Å absorptions are assumed to result in a net transfer from $v_2 = 0$ to 2. For densities $n(H_2) \lesssim 300$ cm^{-3}, radiative pumping can alter the populations in $v_2 = 1$ and 2 levels by up to 100 per cent; but the fraction of interstellar C_3 molecules having excited vibrational levels is *always* negligible unless $n(H_2) \gtrsim 10^5$ cm^{-3}.

In summary, we expect the C_3 molecules to be in the (0, 0, 0) ground vibrational state for which the rotational levels are thermalized. The interstellar line is then a band of partially resolved lines: in particular, the strongest Q-branch lines near 4051.6 Å are unresolved at our resolution. The low rotational constant $B = 0.430$ cm^{-1} leads to the population of several J-levels: $J_{max} = 6$ to 40 K.

In Fig. 1 are shown representative spectra for two stars, ζ Oph and HD 183143, together with synthetic spectra. For ζ Oph, the parameters adopted for the theoretical spectra were $T_{rot} = 22$ K (BD) and $\Delta v = 3.8$ km s^{-1}, the velocity broadening parameter derived for the ζ Oph cloud (Spitzer & Jenkins 1975). Liszt (1979) identified a narrow CO emission line towards ζ Oph having $b = 0.5$ km s^{-1}. Adoption of this parameter would not affect our upper limit, since our projected slit width corresponds to about 10 km s^{-1}. The ζ Oph spectrum represents several shifted and co-added spectra. The HD 183143 spectrum is a multiple exposure providing a resolution of 0.2 Å. The synthetic spectra have been convolved with the appropriate Gaussian-slit profile function. C_3 wavelengths were taken from Gausset *et al.* (1965).

Table 2 shows derived upper limits for the C_3 column density, together with data for other species. Where H I and H_2 measurements are unavailable, the reddening $E(B-V)$ has been converted to $N(H + 2H_2)$ using the relation of Bohlin, Savage & Drake (1978): $N(H + 2H_2) = 5.8 \times 10^{21} E(B-V)$. The fractional abundance $f(C_3)$ is defined as the ratio of $N(C_3)$ to $N(H + 2H_2)$. Since the C_3 is expected to be concentrated in the cool core of the

Table 2. Interstellar molecules.

Star	C_3 limits		N(CO) cm^{-2}	N(H + 2H$_2$) cm^{-2}	f(C_3)
	W_λ (mÅ)	N cm^{-2}			
ζ Oph	4	1.5×10^{12}	1.2×10^{15} ★	1.4×10^{21}	1.1×10^{-9}
ζ Per	10	3.7×10^{12}	7×10^{14} †	1.6×10^{21}	2.3×10^{-9}
HD 23753	9	3.3×10^{12}		1.2×10^{20} §	2.8×10^{-8}
HD 183143	12	4.4×10^{12}		7.3×10^{21} §	6.0×10^{-10}
55 Cyg	10	3.7×10^{12}		3.1×10^{21} §	1.2×10^{-9}
26 Cep	12	4.4×10^{12}	7×10^{14} ‡	3.6×10^{21} §	1.2×10^{-9}

★ Smith, Krishna Swamy & Stecher (1978).
† Snow (1977).
‡ Black (1979).
§ Calculated from $E(B-V)$, see text.

ζ Oph cloud, we can also deduce an upper limit for the value of $f(C_3)$ in the core by taking the BD core prediction: $N(H + H_2) = 5.1\times10^{20}$ cm^{-2}; thus $f(C_3) < 3.0\times10^{-9}$.

The column density of C_3 is likely to be correlated with that of H_2 rather than $(H + H_2)$. However, $N(H_2)$ has only been measured towards two stars in our sample. For ζ Oph and ζ Per we find $N(C_3)/N(H_2) < 2.7\times10^{-9}$ and 7.9×10^{-9}, respectively. Other molecular ratios for the ζ Oph cloud are: $N(C_3)/N(CO) < 1.2\times10^{-3}$ and $N(C_3)/N(C_2) < 0.11$, where the C_2 column density is taken from Erman *et al.* (1981).

4 Insterstellar C_3 chemistry

The abundance of C_3 in diffuse clouds was predicted previously by Mitchell *et al.* (1979). C_3 was considered to form by dissociative recombination of C_3H^+, with the latter formed by reaction of H_2 with C_3^+ (and C^+ with C_2H_2). Destruction of C_3 was by photodissociation to C_2 and C. The adopted gas density and extinction A_V were varied simultaneously, as expected for a cloud of fixed mass and the C_3 abundance was predicted to increase rapidly with increasing density and A_V. C_3 was more abundant than C_2 for $n > 100$ cm^{-3} ($A_V > 0.6$ mag), with $\log f(C_3) = -8.7$ at $n = 100$ and -6.2 at $n = 1000$ cm^{-3}.

In order to examine in more detail the separate dependences on n and A_V, a new series of calculations was performed. The abundances of a large set of species (10 elements and 128 molecules and ions) were calculated in the steady-state approximation for densities $n = 100$ and 1000 cm^{-3} and a range of values of A_V. These calculations were made with a program written by A. G. G. M. Tielens and W. Hagen at the University of Leiden. The large majority of the 1520 reaction rates were taken from Prasad & Huntress (1980) and BD. Elemental depletion factors were those of Morton (1975). Detailed information can be obtained from one of us (RESC) if desired.

Reactions of immediate relevance to C_3 formation and destruction are listed in Table 3, and a sketch of the network of reactions involving C_2 and C_3 is given in Fig. 2. The temperature was taken to be 100 K. The dissociative recombination of C_3H^+ has been assumed to result in three possible product distributions with equal probability. Photodissociation of C_3 may result in the products C_2 $(a^3\Pi_u) + C(^3P)$ or $C_2(X\,^1\Sigma_g^+) + C(^1D)$ (Carter *et al.* 1980). Since the bond energy of C_2–C is 7.5 eV (JANAF 1971), the threshold wavelength is below 1640 Å, but the channel is unknown. The ultraviolet spectrum of C_3 in matrix isolation has been studied down to 1950 Å (Weltner & McLeod 1966); no states above the $^1\Pi_u$ were detected. We adopted the rate recommended for photodissociation of

Table 3. Chemical reaction rates.

Reaction				Rate constant for $T = 100$ K cm^3 s^{-1}
C_2H_2	$+ C^+$	$\rightarrow C_3H^+$	$+ H$	2.7×10^{-9}
C_2H	$+ C^+$	$\rightarrow C_3^+$	$+ H$	1.0×10^{-9}
C_3^+	$+ H_2$	$\rightarrow C_3H^+$	$+ H$	1.0×10^{-9}
C_3H^+	$+ e$	$\rightarrow C_2$	$+ CH$	3.9×10^{-7}
		$\rightarrow C_2H$	$+ C$	3.9×10^{-7}
		$\rightarrow C_3$	$+ H$	3.9×10^{-7}
C_3	$+ h\nu$	$\rightarrow C_2$	$+ C$	$5.0 \times 10^{-11} \exp(-1.7 A_V)$
$C_2H_2^+$	$+ e$	$\rightarrow C_2 + H$	$+ H$	7.7×10^{-7}
C_2H	$+ h\nu$	$\rightarrow C_2H^+$	$+ e$	$1.0 \times 10^{-11} \exp(-2.0 A_V)$
C_2H^+	$+ e$	$\rightarrow C_2$	$+ H$	1.2×10^{-6}
C_2	$+ h\nu$	$\rightarrow C$	$+ C$	$5.0 \times 10^{-11} \exp(-1.7 A_V)$
		$\rightarrow C_2^+$	$+ e$	$1.0 \times 10^{-10} \exp(-2.0 A_V)$
C_2	$+ S^+$	$\rightarrow CS^+$	$+ C$	8.1×10^{-10}

C_2 by BD. Since the ionization potential of C_3 is 12.6 ± 0.6 eV (Drowart, de Maria & Inghram 1958), the photoionization rate is probably slow. Ionization of C_3 by cosmic rays has been included, but it is only significant at high A_V.

Results for C_2, C_3 and CO, as a function of density and extinction, are shown in Fig. 3. C_3 is predicted to vary in a manner similar to C_2 and is a sensitive function of the extinction. These results show *less* C_3 than did Mitchell *et al.* (1979) because of use of different reactions and rates. Using our results together with the BD ζ Oph cloud model, we find $N(C_2) = 2 \times 10^{13}$ cm^{-2} (BD predicted 1.4×10^{13} cm^{-2}). The observed column density is

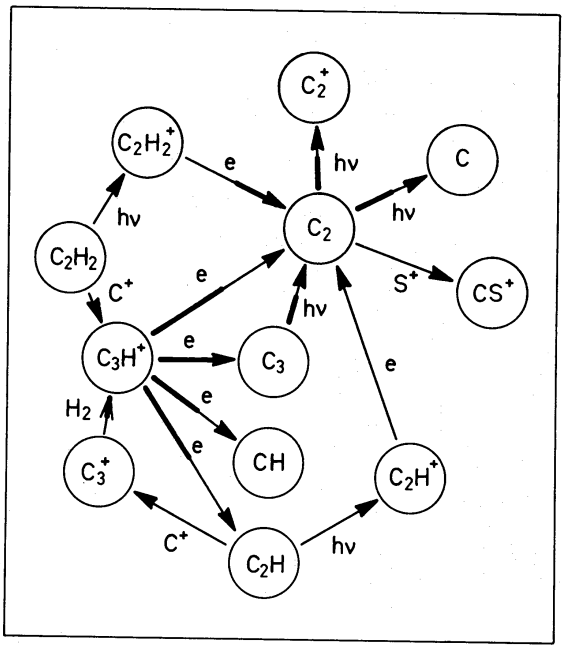

Figure 2. Schematic outline of chemical reactions connected with C_3 and C_2 formation and destruction. Bold line arrow heads or tails indicate dominant formation or destruction paths respectively for the case $A_V = 1, n = 1000$ cm^{-3}.

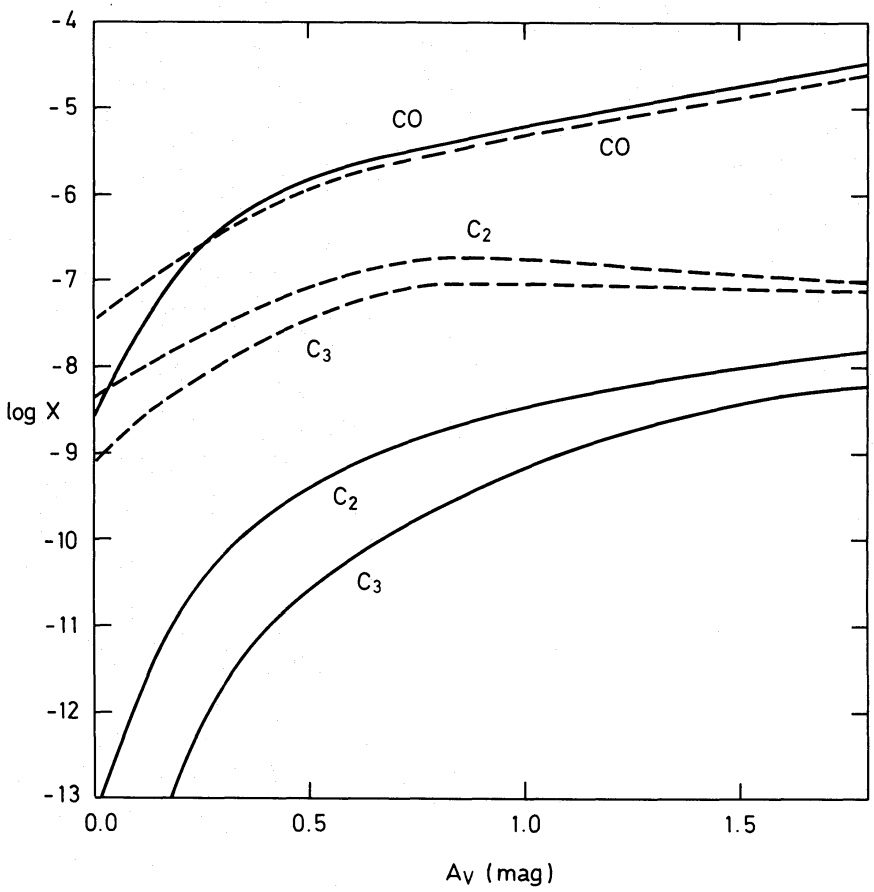

Figure 3. Predicted concentrations of CO, C_2 and C_3 plotted as a function of visual extinction A_V. X is the fractional concentration, $X = n(\text{mol})/n(\text{total})$; note that $X(C_3) \cong f(C_3)$ in Table 2. Solid lines give results for n(total) = 100 cm^{-3}, dashed lines for n = 1000 cm^{-3}. Both calculations are for T_{kin} = 100 K.

1.4×10^{13} cm^{-2} (somewhat dependent on the assumed T_{rot}, Chaffee & Lutz 1978) according to a revised oscillator strength reported by Erman *et al.* (1981). Our predicted C_3 column density for ζ Oph is 7×10^{12} cm^{-2}, a factor of 5 higher than our observed upper limit.

The C_3 abundance is predicted to reach 10^{-7} at the centre of diffuse cloud cores. C_3 should be sought towards stars with $A_V \geqslant 1$ mag and showing evidence of local high-density material (e.g., from CO or H_2 ultraviolet lines). Predicted ratios of C_3 to C_2 depend on several unmeasured reaction rates; this is because the formation paths of each are quite different. Note that in the scheme of Mitchell *et al.* (1979) the main formation channel for C_2 is dissociation of C_3, for $n < 10^3$ cm^{-3} ($A_V \leqslant 3$ mag). In this work and that of BD, recombination of $C_2H_2^+$ or C_2H^+, respectively, are more important.

5 Discussion

C_3 has not yet been detected in diffuse clouds. The upper limits derived in this work are lower than the predictions, by about a factor of 5 for ζ Oph. However, there are sufficient uncertainties in the large chemical schemes which include many unmeasured reaction rates to admit errors at this level. In particular, both the photodissociation rate for C_3 and the rate and product distribution for dissociative recombination of C_3H^+ are unmeasured. The

adopted photodissociation rate corresponds to a transition having $f = 0.003$ at a wavelength of 1500 Å. A rate corresponding to $f \geqslant 0.015$ would bring the predicted C_3 abundance below our observed upper limits. The rate could easily be much larger if a stronger electronic transition is involved; for example, a part of the absorption from the ground state into the $^1\Sigma_u^+$ state, predicted to occur near 1540 Å, may be dissociative.* This transition is predicted to have $f_{el} = 0.92$ (Römelt *et al.* 1978). Clearly, laboratory spectroscopy of C_3 needs to be extended into this wavelength region. A study of the C_3H^+ recombination reaction would also be useful; if the products $C_2 + CH$ or $C_2H + C$ are strongly favoured then the lower formation rate of C_3 would lead to predicted abundances consistent with the observations.

The discrepancy between the upper limit on $N(C_3)$ towards ζ Oph and the prediction for the BD model could also be due to an overestimation of the gas density in the ζ Oph cloud cool core. Crutcher & Watson (1981) have rediscussed the relevant diagnostic observations of atomic and molecular species and concluded that the parameters $n \sim 200\,cm^{-3}$ and $T = 65$ K describe the ζ Oph cloud best. Adoption of this lower density would remove the discrepancy, because the predicted C_3 density is very dependent on the total density (Fig. 3).

Laboratory work must include the measurement of the ionization potential of C_3 and the photoionization cross-section between 911 Å and the threshold wavelength near 983 Å. C_3 has been studied in the infrared region by Treffers & Gilra (1975), who identified the asymmetric stretch ν_3 band near 5 μm. The bending mode ν_2 (0,1,0) – (0,0,0) lines will be near 158 μm and could be measured with gaseous or matrix-isolated C_3. In addition sufficient *ab initio* results may now be available to calculate line strengths for these bands (e.g. Perić-Radić *et al.* 1977; Carter *et al.* 1980; Jungen & Merer 1980).

C_3 may be detected via the 4050 Å band given spectra sufficient to measure features with W_λ of a few tenths of a mÅ. Shulman, Bartolot & Thaddeus (1974) were able to measure interstellar $K1$ lines near 4044 Å having $W_\lambda \sim 0.8$ mÅ from 31 co-added photographic spectra (these spectra do not extend to 4050 Å). We also draw attention to the calculated strengths of the $^1\Sigma_u^+ - {}^1\Sigma_g^+$ band: once laboratory wavelengths are known, an extremely sensitive search for C_3 could be made. The ν_2 (0,1,0) – (0,0,0) band near 158 μm might be detectable in emission from carbon-rich interstellar or circumstellar clouds if the vibrational collision rate with H or H_2 is high enough (an energy $E/k = 90$ K is also required), or in absorption towards infrared sources such as IRC + 10216.

Note added 1982 May

Shinn (1981) has recently detected the $^1\Sigma_u^+ - X\,^1\Sigma_g^+$ transition in a shock-tube experiment. A band with maximum absorption near 1580 Å and an oscillator strength $f_{el} = 0.90$ was observed. It is to be hoped that a rotational analysis of this band will become available, enabling an ultraviolet search for C_3 to be made.

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* Sitko, Savage & Meade (1981) note that the ultraviolet flux of HD 44179, the illuminating star for the Red Rectangle, shows a precipituous decline for $\lambda \lesssim 1600$ Å which they speculate may be a molecular photoionization or photodissociation edge. Is the C_3 molecule responsible for this flux discontinuity? Warren-Smith, Scarrott & Murdin (1981) provide 'marginal evidence' for emission at 4050 Å. Several strong and unidentified features in the red are suspected of having a molecular origin (see also Schmidt, Cohen & Margon 1980).

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References

Becker, K. H., Tatarczyk, T. & Radić-Perić, J., 1979. *Chem. Phys. Lett.*, **60**, 502.
Black, J. H., 1979. In *IAU Symp. 87, Interstellar Molecules,* p. 257, ed. Andrews, B. D., Reidel, Dordrecht, Holland.
Black, J. H. & Dalgarno, A., 1977. *Astrophys. J. Suppl.*, **34**, 405.
Black, J. H., Dalgarno, A. & Hartquist, T. W., 1978. *Astrophys. J.*, **224**, 448.
Bohlin, R. C., Savage, B. D. & Drake, J. F., 1978. *Astrophys. J.*, **224**, 132.
Carter, S., Mills, I. M. & Murrell, J. N., 1980. *J. molec. Spectrosc.*, **81**, 110.
Chaffee, F. H. & Lutz, B. L., 1978. *Astrophys. J.*, **221**, L91.
Chaffee, F. H., Lutz, B. L., Black, J. H., Vanden Bout, P. A. & Snell, R. L., 1980. *Astrophys. J.*, **236**, 474.
Clementi, E. & Clementi, H., 1962. *J. chem. Phys.*, **36**, 2824.
Cooper, D. M. & Jones, J. J., 1979. *J. quantit. Spectros. radiat. Transfer,* **22**, 201.
Crampton, D., Cowley, A. P. & Humphreys, R. M., 1975. *Astrophys. J.*, **198**, L135.
Crutcher, R. M. & Watson, W. D., 1981. *Astrophys. J.*, **244**, 855.
Douglas, A. E., 1977. *Nature,* **269**, 130.
Drowart, J., de Maria, G. & Inghram, M. G., 1958. *J. chem. Phys.*, **24**, 1015.
Erman, P., Lambert, D. L., Larsson, M. & Mannfors, D., 1982. *Astrophys. J.*, **253**, 983.
Gausset, L., Herzberg, G., Lagerqvist, A. & Rosen, B., 1965. *Astrophys. J.*, **142**, 45.
Herbig, G. H., 1968. *Z. Astrophys.*, **68**, 243.
Herbig, G. H., 1975. *Astrophys. J.*, **196**, 129.
Hobbs, L. M., 1974. *Astrophys. J.*, **191**, 395.
JANAF, 1971. *Thermochemical Tables, NSRDS-NBS-37,* US Govt. Printing Office, Washington.
Jungen, Ch. & Merer, A. J., 1980. *Mol. Phys.*, **40**, 95.
Lesiecki, M. L., Hicks, K. W., Orenstein, A. & Guillory, W. A., 1980. *Chem. Phys. Lett.*, **71**, 72.
Liszt, H. S., 1979. *Astrophys. J.*, **233**, L147.
Millikan, R. C. & White, D. R., 1963. *J. chem. Phys.*, **39**, 3209.
Mitchell, G. F., Ginsburg, J. L. & Kurtz, L. J., 1979. *Astrophys. J. Suppl.*, **38**, 34.
Morton, D. C., 1975. *Astrophys. J.*, **197**, 85.
Perić-Radić, J., Römelt, J., Peyerimhoff, S. D. & Buenker, R. J., 1977. *Chem. Phys. Lett.*, **50**, 344.
Prasad, S. S. & Huntress, W. T., 1980. *Astrophys. J. Suppl.*, **43**, 1.
Römelt, J., Peyerimhoff, S. D. & Buenker, R. J., 1978. *Chem. Phys. Lett.*, **58**, 1.
Schmidt, G. D., Cohen, M. & Margon, B., 1980. *Astrophys. J.*, **239**, L133.
Shinn, J. L., 1981. *Paper No. 81-1189, AIAA 16th Thermophysics Conference,* Palo Alto, USA.
Shulman, S., Bartolot, B. J. & Thaddeus, P., 1974. *Astrophys. J.*, **193**, 97.
Sitko, M. L., Savage, B. D. & Meade, M. R., 1981. *Astrophys. J.*, **246**, 16.
Smith, A. M., Krishna Swamy, K. S. & Stecher, T. P., 1978. *Astrophys. J.*, **220**, 138.
Snow, T. P., 1977. *Astrophys. J.*, **216**, 724.
Snow, T. P., 1980. In *IAU Symp. 87, Interstellar Molecules,* p. 247, ed. Andrew, B. H., Reidel, Dordrecht, Holland.
Souza, S. P. & Lutz, B. L., 1977. *Astrophys. J.*, **216**, L49.
Spitzer, L. & Jenkins, E. B., 1975. *A. Rev. Astr. Astrophys.*, **13**, 133.
Swings, P., 1942. *Rev. Mod. Phys.*, **14**, 190.
Swings, P., McKellar, A. & Rao, K. N., 1953. *Mon. Not. R. astr. Soc.*, **113**, 571.
Treffers, R. R. & Gilra, D. P., 1975. *Astrophys. J.*, **202**, 839.
Tull, R. G., Choisser, J. P. & Snow, E. H., 1975. *Appl. Opt.*, **14**, 1182.
Uesugi, A. & Fukuda, I., 1970. *Contr. Inst. Astrophys. Kwasan Obs.*, University of Kyoto, No. 189.
Vogt, S. S., Tull, R. G. & Kelton, P. K., 1978. *Appl. Opt.*, **17**, 574.
Warren-Smith, R. F., Scarrott, S. M. & Murdin, P., 1981. *Nature,* **292**, 317.
Weltner, W. & McLeod, D., 1966. *J. chem. Phys.*, **45**, 3046.
Wilson, R. E., 1953. *General Catalog of Stellar Radial Velocities,* Carnegie Institution of Washington.