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INTERSYSTEM TRANSITIONS OF INTERSTELLAR CARBON MONOXIDE TOWARD ζ OPHIUCHI[1]

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ABSTRACT

Absorption from seven intersystem (triplet-singlet) transitions of interstellar ^{12}CO were detected in ultraviolet spectra of ζ Oph. The observed equivalent widths are approximately consistent with the transitions' predicted *f*-values (Morton & Noreau 1994) and the ^{12}CO column density derived from the weakest of the observed *A–X* bands. These unsaturated intersystem transitions provide the opportunity to measure the ^{12}CO column density for heavily reddened (dense) sight lines. Laboratory measurements of oscillator strengths more precise than available ones will be needed to derive accurate column densities.

Subject headings: ISM: abundances — ISM: molecules — molecular data — ultraviolet: ISM

1. INTRODUCTION

The Goddard High Resolution Spectrograph (GHRS) on the *Hubble Space Telescope* (*HST*) provides the opportunity for obtaining data on weak atomic and molecular lines. Signal-to-noise ratios of 1000 are achievable (e.g., Federman et al. 1993; Lambert et al. 1994b), thereby allowing detection of features with equivalent widths of ~0.3–0.5 mÅ. The value of studying weak lines includes the ability to analyze absorption from species whose other transitions are saturated (Cardelli et al. 1994) and the ability to acquire abundances of rare species (Cardelli et al. 1993; Federman et al. 1993). Here we examine absorption from spin-forbidden (or intersystem) transitions in CO toward ζ Ophiuchi.

Several triplet states of ^{12}CO and ^{13}CO have potential curves that cross the curve for the $A\,^1\Pi$ state (Le Floch, Rostas, & Rostas 1990; Haridass & Huber 1994). These crossings lead to states of mixed character, with the result that transitions between the ground state ($X\,^1\Sigma^+$) and the triplet states are reasonably strong. When the perturbed states are of low rotational quantum number, these intersystem (triplet-singlet) transitions may be sufficiently strong to give observable interstellar lines. Morton & Noreau (1994) compiled a list of the strongest triplet-singlet transitions which involve the *a′*, *d*, and *e* states. Pwa & Pottasch (1986) detected one of the strongest of these transitions, the $a'\,^3\Sigma^+–X\,^1\Sigma^+$ (14–0) band at 1419 Å, in spectra of ζ Oph taken with *IUE*. Morton & Noreau noted the presence of several additional intersystem transitions seen in GHRS spectra. In this *Letter* we report the detection of seven intersystem transitions. Since all but one of these interstellar bands are unsaturated, they provide, in principle, a check on the ^{12}CO column density derived previously from weak bands of the $A\,^1\Pi–X\,^1\Sigma^+$ system for which experimental *f*-values are not concordant. This is a potentially valuable check because the *f*-values of the intersystem transitions are calculated from experimentally determined mixing coefficients and the *f*-values of the stronger *A–X* bands for which experimental results are in good agreement.

2. OBSERVATIONS

The data include four wavelength intervals acquired with grating G160M of the GHRS. The intervals 1252–1293, 1334–1375, and 1442–1488 Å were obtained as part of a study of interstellar CO toward ζ Oph (Lambert et al. 1994b). Details of these spectral observations with high signal-to-noise ratios appear in Lambert et al. Additional data in the vicinity of 1419 Å come from a study of weak interstellar absorption by Cardelli & Ebbets (1994a). These data were obtained in the same manner as those of Lambert et al., i.e., four samples per diode and the FP-SPLIT command were used. Further details on the issue of fixed-pattern noise, which complicates searches for weak absorption, can be found in Cardelli & Ebbets (1994b). Interstellar lines are imposed on an undulating stellar spectrum. A local continuum around each band was defined and the spectrum rectified. We discuss here rectified spectra.

3. RESULTS

Morton & Noreau (1994) noted that electronic transitions between excited triplet states and the ground singlet state occur in spectral regions accessible with the GHRS. Seven of

[1] Based on observations obtained with the NASA/ESA *Hubble Space Telescope* through the Space Telescope Science Institute, which is operated by the Association of Universities for Research in Astronomy, Inc., under NASA contract NASA-26555.

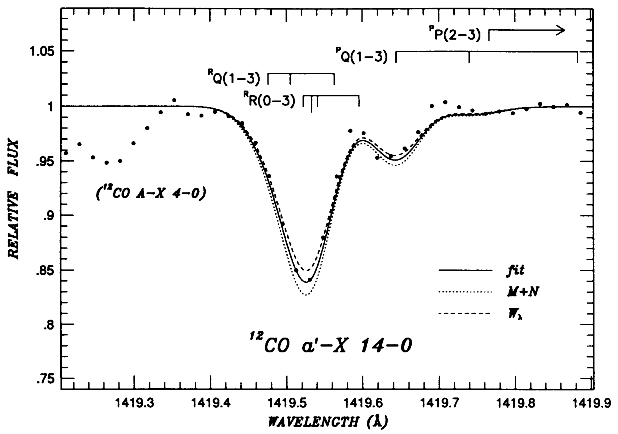

FIG. 1.—Spectrum of the a'–X (14–0) band with fits based on the results of Lambert et al. (1994b) for $N(^{12}CO)$, b-value, and T_{rot}. The dotted curve uses f-values quoted by Morton & Noreau (1994). The solid curve is based on a 13% decrease in f-value to 7.70×10^{-4}. The dashed curve matches the observed W_λ and corresponds to $f_{ISM} = 6.8 \times 10^{-4}$ (see Table 1). The individual lines are indicated, with the longest mark for $J = 0$.

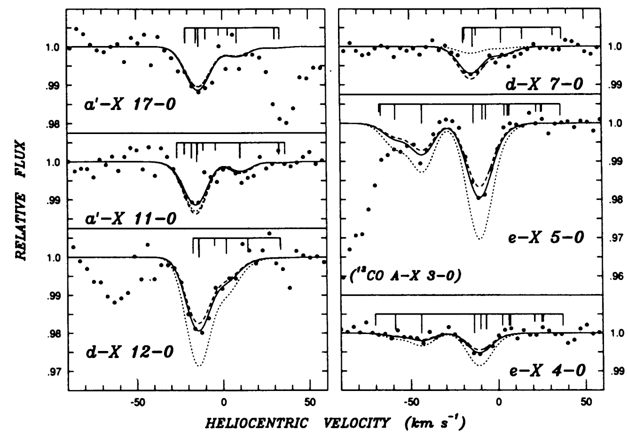

FIG. 2.—Fits to the spectra for the other intersystem bands. The solid curves represent the "best" fit. The dotted curves are based on the f-values quoted by Morton & Noreau (1994), while the dashed curves fit the observed values of W_λ. For a'–X (11–0) the dashed curve lies significantly below the solid one because the observed W_λ includes absorption around 12 km s^{-1} which is somewhat stronger than that expected for $^{P}Q(1)$. The marks show the position of each line; their lengths decrease with increasing J.

these transitions fall within the wavelength intervals covered by our observations: $a'\,^3\Sigma^+$–$X\,^1\Sigma^+$ (17–0) at 1366.2 Å, (14–0) at 1419.5 Å, and (11–0) at 1480.8 Å; $d\,^3\Delta_i$–$X\,^1\Sigma^+$ (12–0) at 1366.4 Å and (7–0) at 1464.1 Å; $e\,^3\Sigma^-$–$X\,^1\Sigma^+$ (5–0) at 1449.5 Å and (4–0) at 1471.2 Å. Even at the moderate resolving power of 20,000 afforded by G160M, structure in these bands beyond the strongest line from $J = 0$ is present. Figures 1 and 2 display the spectra for the observed ^{12}CO bands. The wavelengths in Figure 1 are in the frame of the main interstellar component at $v_{helio} = -15$ km s^{-1}. The procedure for synthesizing the profiles started with the results for ^{12}CO obtained by Lambert et al. (1994b): $N(^{12}CO) = 2.54 \times 10^{15}$ cm^{-2} and $T_{rot} = 4.2$ K from the populations in $J = 0$–3 with $b \sim 0.35$ km s^{-1} for each of two components separated by 1.18 km s^{-1}, as seen in ultrahigh-resolution spectra of CN and CH (Lambert, Sheffer, & Crane 1990). Figure 1 shows the results of the synthesized and observed profiles for the prominent a'–X (14–0) band, which is partially saturated. The figure suggests that the combination of ^{12}CO column density and Morton & Noreau's (1994) f-values is known to an accuracy of $\sim$30%.

Table 1 presents our results. The observed band, the $A\,^1\Pi$–$X\,^1\Sigma^+$ band from which the f-value of the intersystem transition is "borrowed," the wavelength for the strongest line from $J = 0$, the measured equivalent width (W_λ) with 1 σ uncertainties, and the ratio of f-values are indicated. The errors in measured W_λ values include both a statistical (point-to-point) and a continuum fitting uncertainty. The f-values derived from these W_λ values and the ^{12}CO column density are called f_{ISM}, while the f-values in Morton & Noreau (f_{MN}) were derived from mixing coefficients obtained from spectroscopic line positions and the measurements for the allowed A–X transitions by Chan, Cooper, & Brion (1993). With the sole exception of the a'–X (14–0) band, the f-values of these intersystem transitions are smaller than that of the A–X (12–0) band which is the weakest spin-allowed transition yet observed in the interstellar medium.

Figure 2 displays the observational data and the synthesized profiles for the other intersystem transitions. Inspection of Figure 2 and Table 1 shows that the combination of the adopted ^{12}CO column density and Morton & Noreau's f-values does not account satisfactorily for the observed W_λ values of all of these intersystem transitions. For the three a'–X bands, the ratio of Morton & Noreau's f-values to the revised ("interstellar") f-values (f_{MN}/f_{ISM}) is unity to within the combined errors of measurement. Values of f_{MN}/f_{ISM} quite different from unity are found for the other four intersystem bands: the extremes are $f_{MN}/f_{ISM} = 0.2$ for d–X (7–0) and 2.0 for e–X (4–0).

TABLE 1

INTERSYSTEM TRANSITIONS IN ^{12}CO

Band	A-X Band	λ(Å)[a]	W_λ (mÅ)	f_{MN}/f_{ISM}
a'–X (17-0)	6-0	1366.213	1.06 ± 0.21	0.99 ± 0.20
(14-0)	4-0	1419.533	17.46 ± 0.57[b]	1.31 ± 0.07
(11-0)	2-0	1480.789	1.43 ± 0.24	0.94 ± 0.16
d–X (12-0)	6-0	1366.439	1.82 ± 0.22	1.72 ± 0.21
(7-0)	2-0	1464.142	0.94 ± 0.12	0.20 ± 0.03
e–X (5-0)	3-0	1449.544	2.36 ± 0.17	1.89 ± 0.14
(4-0)	2-0	1471.240	0.60 ± 0.12	1.96 ± 0.38

[a] Wavelength of strongest line from $J = 0$; Morton & Noreau 1994 list all lines for each band which were included in our fit.

[b] Pwa & Pottasch 1986 obtained 15.6 mÅ.

4. DISCUSSION

Detection of the intersystem transitions as interstellar bands provides an opportunity to test the accuracy of the predicted f-values. Since the ^{12}CO column density, $N(^{12}CO)$, must be determined independently of these bands in order to test the absolute scale of the f-values, we comment first on $N(^{12}CO)$ as it is derived from observations of the weak bands of the allowed A–X system. Of course, relative f-values of intersystem transitions are independent of $N(^{12}CO)$.

The f-values f_{ISM} are based on $N(^{12}CO) = 2.54 \times 10^{15}$ cm^{-2} derived by Lambert et al. (1994b) from W_λ values of weak ^{12}CO A–X bands measured off *HST* and *Copernicus* spectra with f-values taken from inelastic electron scattering experiments made by Chan et al. (1993). New laboratory measurements of the integrated absorption by these bands (Smith et al. 1994) confirm Chan et al.'s values, as do ab initio predictions

(Kirby & Cooper 1989). For the 11–0 band, the weakest for which an accurate W_λ was available from *HST* spectra, Smith et al. (1994) obtained $f(11\text{–}0) = (1.7 \pm 0.3) \times 10^{-4}$, in good agreement with Chan et al.'s estimate of $f(11\text{–}0) = (1.8 \pm 0.2) \times 10^{-4}$. The weakest band considered by Lambert et al. in the derivation of $N(^{12}CO)$ was the 12–0 band, for which Smith et al. obtain $f(12\text{–}0) = (6.9 \pm 0.8) \times 10^{-5}$ but Chan et al. report $f(12\text{–}0) = (9.0 \pm 1.0) \times 10^{-5}$. Considering the accuracy of W_λ for the 12–0 band which was determined from *Copernicus* spectra (Wannier, Penzias, & Jenkins 1982), the new f-values confirm that $N(^{12}CO) = 2.54 \times 10^{15}$ cm^{-2} to within 20% (1 σ).

This column density differs apparently from two recent estimates, $N(^{12}CO) = 2.2 \times 10^{15}$ cm^{-2} (Sheffer et al. 1992) and 1.8×10^{15} cm^{-2} (Lyu, Smith, & Bruhweiler 1994), based on almost the same observations of the weak A–X ^{12}CO interstellar bands. The differences reflect differences in the adopted f-values of the weakest observed bands. Principal experimental results for the f-values appear to form a bimodal distribution. As already noted, Chan et al.'s results are confirmed now by Smith et al. (1994) and are consistent with ab initio predictions. Three alternative sets of experimental f-values by three different techniques (absorption spectroscopy, electron scattering, and radiative lifetime) are larger than Chan et al.'s values by 40%–60% for the relevant weak A–X bands (Lambert et al. 1994b). There are no decisive reasons for preferring, as we do here, the low over the high f-values for the 11–0 and 12–0 bands. The high f-values do, however, lead to an unphysical curve of growth for the ^{13}CO bands (Lambert et al. 1994b), suggesting that the range spanned by the f-values of the 2–0 to 7–0 bands is larger, as displayed by the low f-values.

Since there are perturbations arising from spin-orbit interactions, the triplet states are mixed slightly with the $A\,^1\Pi$ state (and vice versa), and then the triplet–$X\,^1\Sigma^+$ intersystem transition occurs as an electric dipole (allowed) transition. A calculation of the f-value of these intersystem transitions calls for the mixing coefficients and the f-values of the A–X 2–0 to 6–0 bands from which "intensity is borrowed." The mixing coefficients may be calculated rather precisely from the energy levels of the perturbed triplet and $A\,^1\Pi$ states; for example, Kittrell, Le Floch, & Garetz (1993) claim that their mixing coefficients for the $a'\,^3\Sigma^+$ and $d\,^3\Delta$ states are accurate to better than 1%.

Morton & Noreau (1994) tabulate the predicted f-values based upon the A–X system's f-values measured by Chan et al. (1993). In contrast to the 11–0 and 12–0 A–X bands that determine $N(^{12}CO)$, the f-values of the A–X bands 2–0 to 6–0 determined by other experimenters are in fair agreement: $f_{\rm others}/f_{\rm Chan} = 1.05 \pm 0.1$ according to Lambert et al. (1994b, Table 4) with one exception. Therefore, alternative choices of f-values for the A–X band are expected to change the predicted f-values $f_{\rm MN}$ by no more than a few percent. (The perturbations affect only slightly the f-values of the A–X bands.)

The accuracy of the predicted f-values has been partially tested by accurate measurements of the radiative lifetimes of individual rotational levels of the $a'\,^3\Sigma^+$ ($v = 14$) and $e\,^3\Sigma^-$ ($v = 5$) states (Strobl & Vidal 1987). This data set was reanalyzed by Le Floch et al. (1990), who clearly show that the measured and predicted lifetimes are equal to within a few percent. (Use of Chan et al.'s f-values for the contributing A–X band would not impair this agreement.) These analyses also provide the unperturbed radiative lifetimes of the triplet states which cannot be determined from the perturbed (or unperturbed) energy levels. The unperturbed lifetimes are most probably determined by allowed triplet-triplet transitions (specifically transitions to the $a\,^3\Pi_r$ state) with a negligible contribution from the forbidden transitions to the $X\,^1\Sigma^+$ ground state from the triplet state of interest. The great value of Strobl & Vidal's experiment was that lifetimes were measured for individual rotational levels. For an obvious reason, rotationally unresolved measurements from a group of rotational levels of unknown initial populations are much less useful for testing the predictions; see Le Floch et al., who discuss several series of measurements.

The expectation is that, in general, the predicted f-values of the intersystem transitions should be accurate to about 5%–10% (1 σ), where the uncertainty is likely to be dominated by the f-value of the appropriate A–X band. Morton & Noreau (1994) remark that the uncertainty of the predicted f-values may be larger for some intersystem transitions, especially when multiple interactions are present or the perturbation is very weak so that the intersystem part cannot be ignored.

Interstellar detections of the CO intersystem bands offer an opportunity to make an independent test of the f-value predictions. The derived absolute f-values depend on the adopted $N(^{12}CO)$. The predicted W_λ values of the bands are insensitive to the choice of the excitation temperature because, to within 10% or better, the total f-value from a lower rotational level is the same for the populous levels $J = 0$, 1, and 2. The choice of $T_{\rm rot}$ (=4.2 K) is confirmed, however, by the profiles of the bands, where, for example, the "red" component of the a'–X and d–X bands is set by the $J = 1$ (and $J = 2$) levels and the "blue" or stronger component by the $J = 0$ (primarily) and $J = 1$ components. If $N(^{12}CO)$ is known to about 20%, the values of W_λ of the intersystem bands to about 15%, and the f-values to 5%–10%, we expect $f_{\rm MN}/f_{\rm ISM}$ to be unity to within about 30%. Inspection of Table 1 shows that only the three a'–X bands meet this expectation. The a'–X (11–0) band corresponds to $f_{\rm MN}/f_{\rm ISM} \simeq 1.6$ if the strongest line is fitted (see Fig. 2). For three of the four other bands, $f_{\rm MN}$ is greater than $f_{\rm ISM}$ (1.7–2.0). On the other hand, $f_{\rm MN}$ for the d–X (7–0) band is smaller ($f_{\rm MN}/f_{\rm ISM} \simeq 0.2$), but here mixing coefficients for the $d\,^3\Delta_i$ state are very small.

The ratio $f_{\rm MN}/f_{\rm ISM}$ is dependent on the adopted value of $N(^{12}CO)$. To remove this dependence, we consider relative f-values. If the strongest of the seven bands [a'–X (14–0)] is adopted as the reference band, the relative f-values are $f/f[a'\text{–}X\ (14\text{–}0)] = (0.029,\ 0.038 \pm 0.009)$ for a'–X (17–0), (0.032, 0.037 ± 0.007) for a'–X (11–0), (0.089, 0.067 ± 0.010) for d–X (12–0), (0.111, 0.077 ± 0.008) for e–X (5–0), and (0.027, 0.018 ± 0.005) for e–X (4–0), where the first entry with an expected accuracy of $\pm 10\%$ or better is from Morton & Noreau and the second entry is from our $f_{\rm ISM}$-values. [The obviously discrepant d–X (7–0) band is not listed.] Discrepancies remain that are independent of the choice for $N(^{12}CO)$; for example, the e–X (5–0) band requires $W_\lambda \simeq 3.4$ mÅ, not the measured 2.4 mÅ, in order to be consistent with the measured W_λ of the a'–X (14–0) band and the predicted relative f-values of this pair of bands. Note that Strobl & Vidal's (1987) measured radiative lifetimes are in excellent agreement with predictions for both the $a'\,^3\Sigma^+$ ($v = 14$) and $e\,^3\Sigma^-$ ($v = 5$) states (Le Floch et al. 1990), and hence it is difficult to assign the cause of this particular discrepancy.

These comparisons of $f_{\rm MN}$ and $f_{\rm ISM}$ show that our best estimates of $N(^{12}CO)$ and $f_{\rm MN}$ do not fully account for the observed W_λ values of the interstellar bands. [We discount the d–X (7–0) band, for which we suppose $f_{\rm MN}$ to be in error on account of the very small mixing coefficients and the possibility of "borrowed intensity" from the A–X (3–0) band (A. Le Floch 1994, private communication).] To reconcile f_{MN} and f_{ISM}, it seems necessary to fault one or more of the three controlling factors: $N(^{12}CO)$, f_{MN}, and W_λ. First, adjustment of $N(^{12}CO)$ will *not* change the fact that the relative f-values derived from the W_λ values do not match the predicted values. A 30% reduction in $N(^{12}CO)$ would center the range of the f_{MN}/f_{ISM} ratios on unity. Such a reduction would push the uncertainties assigned by Smith et al. (1994) and Chan et al. (1993) to their measured f-values for the weak A–X bands to their upper limits. We also recall that three alternative sets of experimental f-values for these A–X bands would lower the $N(^{12}CO)$ by 40%–60%. Second, discussions of the prediction of the f-values of intersystem bands convey the impression that the expected errors of the f_{MN} values are substantially below the level implied by the range of f_{MN}/f_{ISM} in Table 1. It may, however, be significant that the magnitude of f_{MN}/f_{ISM} appears correlated with the identity of the triplet state: the three a'–X bands have $f_{MN}/f_{ISM} \sim 1$, but the e–X bands have $f_{MN}/f_{ISM} \sim 2$. Perhaps this is an indication that the a'–X transitions have a larger forbidden (unperturbed) f-value than the e–X transitions. Certainly the unperturbed lifetime of $a'\,^3\Sigma^+$ ($v = 14$) is shorter than that of $e\,^3\Sigma^-$ ($v = 5$) (Strobl & Vidal 1987; Le Floch et al. 1990). Third, our assessment of the likely errors in $N(^{12}CO)$ suggest that the observed values of W_λ may be a source of major error. If unidentified interstellar lines are assumed responsible for the failure of f_{ISM} to equal f_{MN}, at least three bands must be contaminated to a similar level. In view of the correspondence between the observed and predicted band profiles in those several cases where a second and weaker CO line is clearly detectable, we conclude that the bands are free of significant blends. Weak *stellar* features could lead to incorrect placement of the stellar continuum (see Lambert, Sheffer, & Federman 1994a). Reobservation of the bands at the higher resolution afforded by the echelle would allow a secure definition of the interstellar bands despite the presence of unidentified stellar features. Reobservation would also alleviate a concern that systematic effects due, for example, to the granulation of the photocathodes may limit the definition of very weak lines.

5. CONCLUDING REMARKS

Interstellar studies (e.g., van Dishoeck & Black 1989; Federman et al. 1994) are now focusing on more opaque lines of sight in order to bridge the gap between the traditional diffuse clouds and dark clouds; the latter are primarily observed through molecular microwave lines. This trend is made possible by the use of sensitive charge-coupled devices for visible observations and the GHRS for ultraviolet measurements. Since such heavily reddened sight lines contain substantial amounts of molecular gas, many absorption lines that are measured with optical techniques will be very saturated and difficult to interpret. This problem applies to electronic bands of ^{12}CO, including the frequently observed A–X system. Utilizing intersystem transitions offers a way to study this important molecular diagnostic. The a'–X (14–0) band at 1419 Å will be too strong for precise analysis. The other intersystem bands discussed here (see Table 1 and Fig. 2) appear to meet the requirements for useful investigations, as long as spectra with sufficiently high signal-to-noise ratios are obtained. These other bands are expected to be weak, thereby lessening the uncertainties associated with component structure that is apparent in spectral measurements acquired at ultrahigh resolution. GHRS measurements of these bands should allow $N(^{12}CO)$ and T_{rot} to be established more accurately than is possible from all but the weakest A–X transitions, but the present analysis suggests that precise laboratory or theoretical f-values are needed for the intersystem (and the weakest A–X) bands before accuracies approaching 10% for $N(^{12}CO)$ are possible.

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