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VIBRATIONALLY EXCITED H_2, HCl, AND NO^+ IN THE DIFFUSE CLOUDS TOWARD ζ OPHIUCHI[1]

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ABSTRACT

Absorption lines from vibrationally excited H_2 and from HCl were detected in the ultraviolet spectrum of ζ Oph with the *Hubble Space Telescope.* Improved upper limits on NO^+ absorption were obtained as well. The data were analyzed with an updated version of a chemical model for diffuse clouds (van Dishoeck & Black 1986) as a guide to understanding this gaseous environment. The comparisons suggest that the flux of ultraviolet radiation impinging on the cloud surface is ~1–2 times the average interstellar radiation field, which is lower than once believed.

Subject headings: ISM: molecules — stars: individual (ζ Ophiuchi) — ultraviolet: ISM

1. INTRODUCTION

Knowledge of the density, temperature, and radiative flux permeating interstellar clouds is important for understanding the evolution of interstellar material. Detailed chemical models provide one means of extracting the physical conditions from observations. Observations of species that have low relative abundances place needed constraints on the models. The Goddard High-Resolution Spectrograph (GHRS) on the *Hubble Space Telescope* (*HST*) has the capability to detect weak absorption from rare species (e.g., Cardelli et al. 1993a; Federman et al. 1993). Here, absorption lines from vibrationally excited H_2 and from the less abundant species HCl and NO^+ are examined with the aid of the chemical model first described by van Dishoeck & Black (1986) and updated here.

Previous analyses of excited H_2 in diffuse clouds were mainly based on observations of rotational levels in the ground vibrational state. Spitzer, Cochran, & Hirschfeld (1974) presented data from the *Copernicus* satellite toward 28 stars. Subsequent measurements by Frisch & Jura (1980) yielded absorption from rotationally excited H_2 toward additional stars. Other measurements of rotationally excited H_2 with *Copernicus* included the studies of Frisch (1980) and Allen, Snow, & Jenkins (1990). A rocket-borne experiment (Jenkins et al. 1989) detected high-lying rotational levels at high spectral resolution. Frisch & Jura (1980) also presented upper limits on absorption from the $v = 1$ state. Our measurements, therefore, represent the first interstellar detections of ultraviolet absorption from vibrationally excited H_2.

Several mechanisms can lead to detectable amounts of vibrationally and rotationally excited molecular hydrogen. First, when H_2 forms on a grain surface, some of the excess energy from the recombination of two hydrogen atoms can go into internal energy of the molecule. At the present time it is not clear whether the new molecule becomes vibrationally cold and rotationally hot—states with low v and high J are populated—as suggested by Hunter & Watson (1978) or whether the opposite situation arises (see Duley & Williams 1986, 1992). From his interpretation of absorption from high-lying rotational levels of H_2 in the ground vibrational state, Wagenblast (1992) concluded that the formation process results in rotationally hot molecules. Second, after excitation of an H_2 molecule into its B and C electronic states through the absorption of ultraviolet photons, the molecule will decay radiatively back to the ground electronic state. The emission associated with such decays was observed from IC 63 by Witt et al. (1989) and from the general interstellar medium by Martin, Hurwitz, & Bowyer (1990). Some of this fluorescence leads to dissociation when it terminates in the vibrational continuum of the ground state (Stecher & Williams 1967). The other decays populate various bound excited vibrational states, and through further radiative transitions, cascades toward the vibrational ground state occur (Black & Dalgarno 1976). If this process dominates, estimates of the strength of the far-ultraviolet field are possible (Jura 1975; Black & Dalgarno 1977; van Dishoeck & Black 1986; Black & van Dishoeck 1987; Sternberg 1988; Viala, Roueff, & Abgrall 1988). A third mechanism involves shock excitation where collisions at elevated temperatures take place (e.g., Draine 1986). Van Dishoeck & Black (1986) suggested that observations of lines arising in $v > 0$ can distinguish between the latter two mechanisms, since weak nondissociating shocks are unable to produce detectable amounts of vibrationally excited H_2, whereas fluorescent pumping naturally yields large H_2 populations in high vibrational levels. Our data form tests of the predictions of these models and provide insights into the physical conditions for the gas toward ζ Oph.

Knowledge of the abundances of HCl and NO^+ tests predictions of chemical models. In cloud envelopes, HCl is expected to be one of the most abundant neutral chlorine species (Dalgarno et al. 1974; Jura 1974; Jura & York 1978; van Dishoeck & Black 1986). The abundance of HCl is especially interesting from a chemical perspective. The formation of HCl is initiated through reactions involving Cl^+ and H_2; among the abundant elements whose dominant form is the singly ionized atom, this type of reaction occurs on nearly every collision only for chlorine (Anicich 1993). HCl has been detected in

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dense molecular clouds by Blake, Keene, & Phillips (1985) and was subsequently observed to be widespread by Schilke, Phillips, & Wang (1995) and Zmuidzinas et al. (1995). Of the nitrogen compounds, CN (e.g., see references in Table 9 of Federman et al. 1994) and NH (Meyer & Roth 1991) are observed via absorption from cloud envelopes. Estimates of the amount of NO^+ allow additional constraints to be placed on the nitrogen chemistry.

2. OBSERVATIONAL RESULTS

The observations consist of spectra acquired with the GHRS and its moderate-resolution grating G160M over the wavelength intervals 1252–1293 Å, 1334–1375 Å, and 1442–1488 Å. For each observation, the individual FP-SPLIT subexposures first were corrected for fixed pattern noise/granularity (see Cardelli et al. 1993b, 1994; Cardelli & Ebbets 1994; Fitzpatrick & Spitzer 1994; Lambert et al. 1994 for details) and subsequently were merged in wavelength space. In the majority of cases, the noise in the merged spectrum is photon limited. However, on rare occasions, some isolated weak ($\leq 2\ \sigma$) remnant noise features can be present (see Cardelli & Ebbets 1994). These features generally can be easily identified in the original subexposures and thus are unlikely to be misidentified as spectral features. However, when assigning an identification to any weak feature, some caution in any case must be taken. Since such occurrences are rare, the probability of positive detection must be given added weight if it is at the expected wavelength, as are the H_2 and HCl lines reported here. Furthermore, the H_2 and HCl lines are the strongest ones expected at these wavelengths.

Lines from vibrationally excited H_2 ($v'' > 0$), from the (0–0) band of the electronic transition $C\ ^1\Pi - X\ ^1\Sigma^+$ in HCl, and from the (0–0) and (1–0) bands of the $A\ ^1\Pi - X\ ^1\Sigma^+$ transition in NO^+ fall within the spectral range covered by our observations. Tentative (2–2.5 σ) first detections of the $R(0)$ and $R(1)$ lines in the (0–3) Lyman band ($B\ ^1\Sigma_u^+ - X\ ^1\Sigma_g^+$) of H_2 and of the $R(0)$ line in the C–X (0–0) band of HCl are found at $v_{\text{helio}} = -15$ km s^{-1}, the main interstellar component toward ζ Oph. These are reported in Table 1, along with upper limits for the (0–4) $R(2)$ line and (0–6) $R(2)$ and $R(3)$ lines of the H_2 Lyman band. The (0–6) $R(1)$ line is blended with a line from Ni II and is not included. The line, its wavelength (Abgrall et al. 1993 for H_2), and its equivalent width (W_λ) are indicated in Table 1. The resulting H_2 column densities shown in Table 2 are based on the transition probabilities published by Abgrall et al. (1993).

TABLE 1

OBSERVATIONAL RESULTS

Species	Line	λ (Å)	W_λ (mÅ)
H_2	B–X (0–3) $R(0)$	1274.537	0.34 ± 0.16
H_2	B–X (0–3) $R(1)$	1274.922	0.33 ± 0.16
H_2	B–X (0–3) $R(2)$	1276.325	≤0.30
H_2	B–X (0–4) $R(2)$	1335.131	≤0.70
H_2	B–X (0–6) $R(2)$	1456.076	≤0.15
H_2	B–X (0–6) $R(3)$	1458.132	≤0.15
HCl	C–X (0–0) $R(0)$	1290.257	0.57 ± 0.24
NO^+	A–X (0–0) $R(0)$	1368.197	≤0.34
NO^+	A–X (1–0) $R(0)$	1339.636	≤0.34
UID	...	1270.96[a]	0.75 ± 0.19
UID	...	1346.54[a]	1.73 ± 0.36

[a] Wavelength scale set under the assumption that the absorption arises from the main interstellar component at $v_{\text{helio}} = -15$ km s^{-1}.

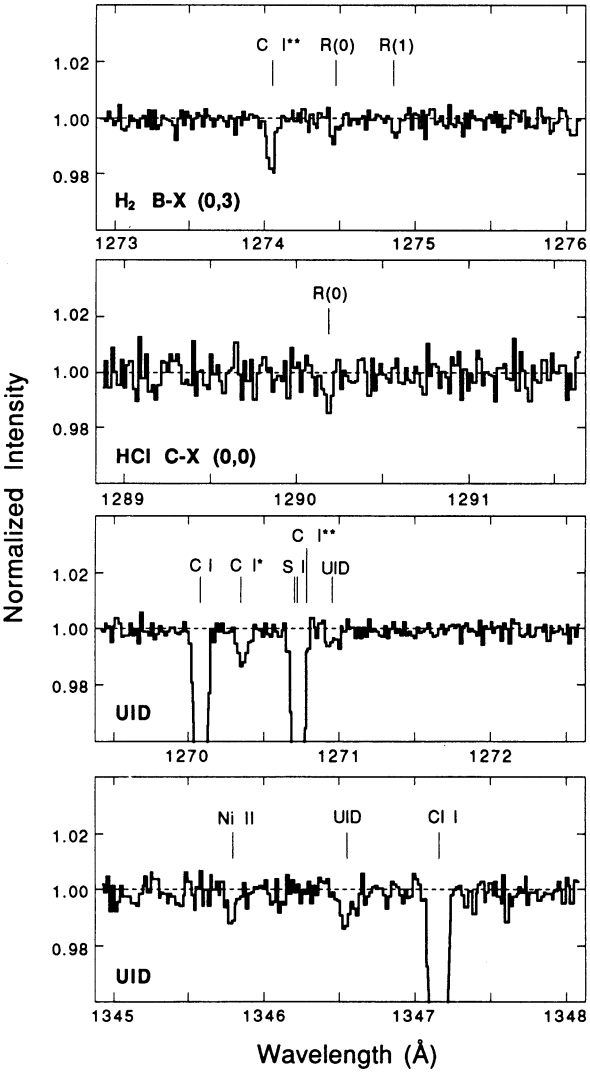

FIG. 1.—Newly detected lines toward ζ Oph. All features are identified in the wavelength frame of the main interstellar component at $v_{\text{helio}} = -15$ km s^{-1}. The bottom two panels show features of unknown origin.

Table 1 also presents upper limits for the $R(0)$ line of the A–X (0–0) and (1–0) bands of NO^+ and values of W_λ for two unidentified lines not previously noted. In all, there are only four unidentified features in ~150 Å covered by our measurements which have S/N's ranging from 200 to nearly 1000. The other two are described in Cardelli, Savage, & Ebbets (1991) and Tripp, Cardelli, & Savage (1994). The lines/features discussed here are shown in Figure 1. The lines of C I, S I, Cl I, and Ni II noted in the figure were discussed in papers on *Copernicus* results (Morton 1975) and other *HST* results (e.g., Federman et al. 1993).

3. INTERPRETATION

Model G in van Dishoeck & Black (1986), which was previously considered by them to be the best representation for the diffuse gas toward ζ Oph, was updated in light of recent developments. The Doppler parameter b for the H_2 lines was lowered from 3.0 to 0.75–1.0 km s^{-1}, as suggested by GHRS data on neutral atoms (e.g., Savage, Cardelli, & Sofia 1992; Federman et al. 1993). Although ultra–high-resolution data

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TABLE 2

THEORETICAL PREDICTIONS

Species	Model G[a]	Model G1[b]	Model G2[c]	Model G3[d]	Observations
I_{UV}[e]	3.5	2.2	2.2	2.2	
b-value	3.0	1.0	1.0	1.0	
H_2	4.2 (20)	4.2 (20)	4.2 (20)	4.2 (20)	(4.2 ± 0.3) (20)
H_2 $v = 0$:					
$J = 5$......	4.5 (14)	1.9 (14)	0.9 (14)	1.9 (14)	(4.3 ± 0.5) (14)
$J = 6$......	5.3 (13)	2.2 (13)	1.7 (13)	2.6 (13)	(4.9 ± 0.5) (13)
$J = 7$......	3.8 (13)	1.4 (13)	2.2 (12)	1.1 (13)	(3.6 ± 0.4) (13)
H_2 $v = 1$:					
$J = 0$......	2.3 (12)	1.0 (12)	1.3 (12)	1.0 (12)	≤7.0 (12)
$J = 1$......	5.5 (12)	2.5 (12)	2.5 (12)	2.5 (12)	≤1.2 (13)
$J = 2$......	6.0 (12)	2.7 (12)	3.5 (12)	2.7 (12)	≤1.0 (13)
H_2 $v = 2$:					
$J = 0$......	9.5 (11)	4.3 (11)	6.0 (11)	4.3 (11)	≤4.4 (12)
$J = 1$......	2.2 (12)	1.0 (12)	1.0 (12)	1.0 (12)	...
$J = 2$......	2.4 (12)	1.1 (12)	1.4 (12)	1.1 (12)	...
H_2 $v = 3$:					
$J = 0$......	5.3 (11)	2.4 (11)	3.2 (11)	2.4 (11)	(2.7 ± 1.3) (11)
$J = 1$......	1.2 (12)	5.7 (11)	5.6 (11)	5.6 (11)	(3.8 ± 1.8) (11)
$J = 2$......	1.3 (12)	5.9 (11)	7.8 (11)	5.8 (11)	≤3.8 (11)
H_2 $v = 4$:					
$J = 0$......	3.4 (11)	1.6 (11)	1.6 (11)	1.6 (11)	...
$J = 1$......	7.3 (11)	3.5 (11)	3.5 (11)	3.5 (11)	...
$J = 2$......	7.9 (11)	3.6 (11)	7.2 (11)	3.6 (11)	≤5.9 (11)
H_2 $v = 6$:					
$J = 0$......	1.7 (11)	7.6 (10)	4.6 (11)	7.6 (10)	...
$J = 1$......	3.4 (11)	1.7 (11)	1.7 (11)	1.7 (11)	...
$J = 2$......	3.6 (11)	1.7 (11)	1.7 (11)	1.7 (11)	≤1.6 (11)
Cl	1.0 (14)	...	...	2.9 (14)	(3.0 ± 1.0) (14)
Cl^+	2.6 (12)	...	...	6.5 (12)	(2.0 ± 1.0) (13)
HCl	2.4 (11)	...	...	2.1 (11)	(2.7 ± 1.0) (11)
HCl^+	4.0 (10)	...	...	1.5 (11)	...
NO^+	...	...	...	1.2 (8)	≤8.2 (13)

NOTE.—Table entries are to be read as follows: 4.2 (20) = 4.2×10^{20} cm^{-2}.

[a] From van Dishoeck & Black 1986, using the formation model with 1.5 eV distributed statistically.

[b] Based on H_2 formation model with 1.5 eV distributed statistically.

[c] Based on Duley & Williams 1986: formation in $v = 6, J = 0$ and 1 with $T_{\rm form} = 15$ K.

[d] Based on Wagenblast 1992: formation with fraction 0.73 in $v = 5, J = 9$ and 0.27 in $J = 10$.

[e] I_{UV} is the enhancement factor for the strength of the ultraviolet radiation field.

(Lambert, Sheffer, & Crane 1990; Crawford et al. 1994) reveal $b \sim 0.3$ km s^{-1} for CH and CN, H_2 is more widespread and its line broadening should more closely resemble that of the atomic species. This change in b-value mainly decreases the amount of photon pumping because the lines leading to excitation and dissociation become optically thick to absorption more easily. The extinction curve was taken to be that of ζ Oph according to the parametrization of Fitzpatrick & Massa (1988) instead of the standard curve. Since the curve for ζ Oph is steeper than the average one at far-ultraviolet wavelengths, the amount of pumping is reduced further, as are the rates for photoionization and photodissociation. Total cloud thickness was not varied because it is set by the observed column density of H_2. Since the vibrationally excited H_2 is formed mostly in the outer, small layer of the cloud, the cloud thickness has little effect on its column. All models were based on $A_V \sim 0.8$ mag. Several important reaction rates in the chlorine chemistry were also revised. The laboratory cross sections for chlorine photoionization (Ruščić & Berkowitz 1983) and for HCl photoionization (Frohlich & Glass-Maujean 1990) were used. The calculations by Pradhan, Kirby, & Dalgarno (1991) on HCl^+ photodissociation cross sections were included. All photorates were based on the interstellar radiation field described by Draine (1978). The revised rate coefficients from reactions involving protons and Cl (Pradhan & Dalgarno 1994) and C^+ and HCl (Rebrion et al. 1988) were incorporated into the model. The main uncertainty in the chemical network remains the branching ratio to HCl in the dissociative recombination of H_2Cl^+, which was kept at 0.1 (Smith & Adams 1981).

Although the detections for the lines of H_2 and HCl are at the 2–2.5 σ level, the measurements still provide important constraints for chemical/physical models of the diffuse clouds toward ζ Oph. The equivalent widths for the $R(0)$ and $R(1)$ lines of the H_2 (0–3) Lyman band are ∼0.30 mÅ, a factor of 2–3 smaller than the original predictions of van Dishoeck & Black (1986) for model G and up to a factor of 7 for other models. In their models, the vibrationally excited states are populated primarily via the photon-pumping process. Thus, estimates for the flux of ultraviolet radiation permeating the cloud are obtainable from the amount of H_2 in excited vibrational states. Since our measured values of W_λ are significantly smaller than the predictions of van Dishoeck & Black, one possibility is that the flux is less intense than previously believed.

The populations of levels $J = 0$ and 1 in the $v = 3$ state are only weakly affected by the specific grain surface formation model. Steady state calculations were run that treated the initial distribution upon H_2 formation according to several different models (see also Black & van Dishoeck 1987). In the first case (G1), 1.5 eV of energy was distributed statistically over the various vibration-rotation levels. In the second case (G2), the model of Duley & Williams (1986, 1992) was taken with all molecules formed in $v = 6, J = 0$ and 1 with $T_{\rm form} = 15$ K—vibrationally hot and rotationally cold. In the third model (G3), the molecules were formed rotationally hot in $v = 5$, $J = 9$ and 10 (cf. Wagenblast 1992, after Hunter & Watson 1978).

The results of these calculations are shown in Table 2 for a radiation field that is about a factor of 2 larger than the standard field, the maximum value allowed by the observed $v = 3$ populations. Compared with the statistical distribution, the considerations of Duley & Williams lead to a strong reduction in the amount of rotational excitation in $v = 0$, but to little change in the excited vibrational populations, except in the specific $v = 6$, $J = 0$ level into which most of the formation occurs. The $J = 0$ and 2 level populations for $v \leq 6$ are enhanced by $\sim 30\%$ because there are more cascades from levels with higher v. The use of the formulation by Wagenblast yields higher rotational populations for $v = 0$ and a slight decrease for populations in the lower J levels of the $v > 0$ states. Note that detailed comparison with the results of Wagenblast (1992) is hampered by the fact that his model was time dependent, although such effects are not expected to be significant for the vibrationally excited populations for $t \geq 10^6$ yr. Unfortunately, Wagenblast did not tabulate any predictions for $v > 0$. The best correspondence with our observations involves using the Wagenblast model with a reduction in the ultraviolet flux from one that is ~ 4 times that of Draine's (1978) interstellar field in the original model to one that is 1–2 times as strong. Inclusion of the effects of line overlap in the radiative transfer (cf. Abgrall et al. 1992) could increase this value slightly. The revised flux is now similar to one considered by Federman et al. (1994) in their analysis of C_2 and CN chemistry, and it lessens the discrepancy between predicted and observed CO and CN column densities. However, our inferred scaling factor for the radiation field is still considerably higher than the value of 0.1 inferred by Wagenblast (1992).

Our modeling efforts now produce too little H_2 in high-lying rotational levels for $v = 0$ compared with observations. Time-dependent effects (Wagenblast 1992) may produce more excitation at early times (less than 10^6 yr) given the appropriate initial conditions. These levels could also be populated in heated gas behind a shock (Draine 1986; Heck et al. 1993) or in a turbulent medium. Such conditions, however, are not effective in populating excited vibrational states. If levels up to $J = 5$ could have larger populations by some other mechanism, subsequent ultraviolet pumping out of these levels could enhance $J = 6$ and 7. It is possible that rotationally excited H_2 probes the material responsible for the broad CH^+ line.

The measured column densities in $v = 3$, $J = 0$ and 1 permit direct estimates of intensities of the infrared vibration-rotation emission lines that arise in these levels. The strongest of these emission lines are (3–2) $O(2)$, $Q(1)$, and $O(3)$ at 2.7–3.2 μm and (3–1) $O(2)$, $Q(1)$, and $O(3)$ at 1.3–1.4 μm. The corresponding lines of the (3–0) band are approximately a factor of 0.1 times as strong. The strongest lines of the (3–2) and (3–1) bands will all have fluxes $f_\nu \approx 30(R/2000)[\Omega/(10^{-9}\ \text{sr})]\ \mu$Jy, where R is the resolving power and Ω is the solid angle of the aperture of the spectrograph. Such weak lines are probably not detectable.

Our tentative detection of HCl helps to provide constraints on chemical models of the diffuse clouds toward ζ Oph. The GHRS observations indicate that $W_\lambda \simeq 0.57$ mÅ, which is significantly below the limit of 1.9 mÅ set by measurements with the *Copernicus* satellite (Wright & Morton 1979). Use of the recently refined f-value for the $R(0)$ line of the C–X (0–0) transition, $f = 0.141 \pm 0.020$ (P. Smith 1994, private communication), yields a column density for HCl of 2.7×10^{11} cm^{-2}. The value is in excellent agreement with the original predictions of van Dishoeck & Black (1986), $(2.1\text{–}3.0) \times 10^{11}$ cm^{-2}, and with those from the updated model—see Table 2. The comparison between predictions and observations also included the atomic chlorine species. The column densities for Cl I and Cl II are derived from the observational results of Morton (1975) for Cl I λ1097 and Cl II λ1071 and of Lambert, Sheffer, & Federman (1995) for Cl I λ1347 in conjunction with a curve-of-growth analysis based on the Cl I f-values of Schectman et al. (1993), the Cl II f-value suggested by Morton (1991), and a b-value of 1.2–1.5 km s^{-1} (Federman et al. 1993). Although the experimental f-values of Schectman et al. are larger than previous ones, a recent large-scale calculation by Biémont, Gebarowski, & Zeippen (1994) is consistent with these larger values, provided that the upper state designation for λ1097 is changed to $3d\,^2F_{5/2}$. The model results that include a reduction in flux (to account for our H_2 results) and chemical rates reproduce the data quite well as long as chlorine is essentially undepleted. The sole exception is Cl II, whose predicted column density is below the observed one. Saturation of the weak line λ1071 is not a problem, but contaminating absorption from the H II region surrounding ζ Oph could explain the differences between modeling and observational results.

Our upper limit for absorption from NO^+ is a significant improvement over the previous one ($W_\lambda \leq 5.7$ mÅ; Morton 1975). Yet the new limit is still not sufficient to test the predictions of chemical models in an adequate way. With an f-value of 2.5×10^{-4} for the $R(0)$ line (Hesser 1968), which is consistent with the integrated cross section obtained by electron impact excitation of NO (Ajello et al. 1989), $N(NO^+)$ is $\leq 8.2 \times 10^{13}$ cm^{-2}, a value five orders of magnitude above the predictions of Black & Dalgarno (1977) and those calculated here. The model NO^+ column densities are low because the ion is rapidly removed by dissociative recombination and because there are no efficient formation routes in diffuse clouds other than through photoionization of NO.

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