COSMIC RAY–INDUCED CHEMISTRY TOWARD PERSEUS OB2

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ABSTRACT

New measurements of absorption from interstellar OH at 3078 and 3081 Å are presented for three directions toward the Perseus OB2 association. The measured equivalent widths are in excellent agreement with previous determinations for o and ζ Per. Our measurements also provide stringent upper limits for the line of sight to ξ Per. The available data on 3078 toward o and ζ Per with published equivalent widths for the (0, 0) band of the D–X electronic transition near 1222 Å are used to determine the oscillator strength for the D–X band; the value agrees with theory. The first ground-based detections of absorption from interstellar Ti II λ3072 are discussed in an appendix.

Cosmic-ray ionization followed by ion-molecule reactions is found to be the primary means of producing OH and HD in the environment probed by our observations. Our OH data are used in conjunction with a simple but adequate chemical model to obtain estimates of the cosmic-ray ionization rate. These estimates then yield a value for the local interstellar D/H ratio of (1.5 ± 0.5) × 10−5 from available observations of HD that is consistent with more direct measures. Furthermore, the derived rate allows us to place limits on the production of NH through gas-phase processes.

Subject headings: cosmic rays — ISM: abundances — molecular processes — open clusters and associations: individual (Perseus OB2)

1. INTRODUCTION

Cosmic rays are an important source of ionization for the interstellar medium. This ionization provides the heating for dark molecular clouds (see, e.g., Goldsmith & Langer 1978), and it drives the ion-molecule chemistry for atoms whose ionization potential is greater than hydrogen's. In particular, the chemistries of D-, N-, and O-bearing molecules are initiated by cosmic-ray ionization. In the present paper, new data on OH absorption are used to derive the ionization rate toward o, ζ, and ξ Per. Our determinations then are used to examine the consequences this rate has on the chemistries of HD and NH.

Cosmic ray–induced chemistry toward o, ζ, and ξ Per was studied previously through then available OH and HD observations. Black, Hartquist, & Dalgarno (1978) determined the cosmic-ray ionization rate toward ζ Per, while Hartquist, Doyle, & Dalgarno (1978) determined the rate along the line of sight to o Per. Both determinations were based on measurements of OH absorption. More refined models for these two sight lines were presented by van Dishoeck & Black (1986). Hartquist et al. also obtained an estimate for the ionization rate toward ζ Per from HD observations under the assumption that the elemental abundance of D equals 1.8 × 10−5. More recently, Heck et al. (1993) have modeled the gas toward o Per, and Wagenblast et al. (1993) have considered models for the material toward ζ Per.

Our analysis differs in several important ways from these analyses. Foremost, high-quality atomic data acquired with the Hubble Space Telescope are now available. Second, other available data, such as HD measurements with the Copernicus satellite, are treated in a self-consistent way; for instance, curves of growth based on a common set of b-values for all species in the neutral gas are used to determine column densities. Third, the physical conditions derived from C2 and CN chemistry (see Federman et al. 1994) place additional constraints on the physical conditions for the gas probed by OH and HD.

Here is the outline for the remainder of the paper. The next section presents the observational results on OH, and it is followed by our chemical analysis. The discussion section includes a comparison of the available models for the sight lines toward our program stars as well as our conclusions. Two appendices provide details of the chemical model used here and give results on Ti II absorption at 3072 Å.

2. OBSERVATIONS

The measurements were obtained with the coudé spectrograph of the 2.7 m telescope at McDonald Observatory during 1995 January. A grating was used in second order, providing a dispersion of 0.058 Å pixel−1 in the vicinity of 3080 Å. A combination of CuSO4 and UG-11 filters blocked the stellar flux in first order. The spectra were imaged onto a Tektronix 512 × 512 CCD. A slit width of 240 μm was chosen so that ~2 pixels were sampled along the dispersion axis; this was confirmed by measures of the FWHM (2.2 pixels) for lines from an iron-neon hollow-cathode lamp, which was used for wavelength calibration. Flat fields were obtained to remove pixel-to-pixel sensitivity in the spectral images.

The data were reduced with NOAO's IRAF package in a standard manner. The stellar images were corrected for DC bias and dark current and were flat-fielded. Scattered light,
which was not significant, was removed before aperture extraction as well, and the extracted spectra were placed on a wavelength scale from lines in the Fe-Ne lamp. The spectra in the vicinity of the OH lines at 3078 and 3081 Å within the $A 2{^2}Σ^+ - X 2{^2}Π (0, 0)$ band are shown in Figure 1 for the three lines of sight, $\alpha$, $\zeta$, and $\zeta$ Per. The stellar continuum and the blaze function of the grating were removed in order to produce rectified spectra whose continua were normalized to unity. Doppler shifts were applied to the stellar spectra so that the wavelength scale corresponded to the local standard of rest. These final spectra are the result of observing each star for 7–12 hr, yielding signal-to-noise ratios of 200–400. Table 1 presents the measured quantities from the spectra.

In Table 1, the wavelength for the line, the rotational transition, the equivalent width $W_r$, the velocity in the local standard of rest $v_{\text{LSR}}$, the line oscillator strength, and the OH column density, $N_{\text{A}}(\text{OH})$, for the appropriate $\Lambda$-sublevel are given. Our values for $W_r$ are in excellent agreement with previous results, namely, those of Crutcher & Watson (1976a) for $\alpha$ Per and of Chaffee & Lutz (1977) for $\zeta$ Per, which are given in the notes to Table 1. Upper limits for $W_r$ are based on $3 \sigma$ statistical uncertainties. The value for $v_{\text{LSR}}$ of the lines $Q_{11}(3/2)$ and $Q_{21}(3/2)$ is based on the weighted mean wavelength of the blend. The LSR velocities for the lines seen toward $\alpha$ and $\zeta$ Per do not differ appreciably from the velocity obtained from OH absorption (see, e.g., Federman 1982). The differences are due to the coarse resolution of the present measurements ($\sim 12$ km s$^{-1}$). The line oscillator strengths are derived from the band oscillator strength given by Wang & Huang (1980) $(1.09 \pm 0.04) \times 10^{-5}$ and HönL-London factors that include the effects of intermediate coupling. Wang & Huang based their analysis on the lifetime for the upper state in the $A-X (0, 0)$ band measured by German (1975a). The lifetime measurements of German (1975b) and Dimpf & Kinsey (1979) agree extremely well with those of German (1975a). Table 1 indicates the sum of oscillator strengths for $Q_{11}(3/2)$ and $Q_{21}(3/2)$. It should be noted that the blend $Q_{11}(3/2)$ and $Q_{21}(3/2)$ arises from the $A$-sublevel with $f$ parity, while the $P_{11}(3/2)$ line comes from the sublevel with $e$ parity. A curve-of-growth analysis with a $b$-value of 2 km s$^{-1}$ (see CH results of Federman 1982 and Crane, Lambert, & Shepher 1995) was used to determine column densities, but the linear approximation provides similar results for these weak lines. The values listed for column density in Table 1 are based on the weighted average of all available data for $W_r$. The results for each $\Lambda$-sublevel are consistent with the assumption of equal populations; their sum appears in Table 3 as the total column density for OH. The value for $\alpha$ Per in Table 3 is constrained by the upper limit for $\lambda 3081$.

### 3. Analysis and Results

The present analysis is restricted to gas-phase synthesis of OH, HD, and NH which is initiated by cosmic-ray ionization. It then proceeds via ion-molecule reactions and dissociative electron recombination. Since the ion-molecule schemes are relatively well understood, the analysis can provide constraints on other production routes, such as NH formation on grain surfaces.

The ion-molecule chemistry for OH is described in detail by Glassgold & Langer (1976). The route to OH production

<table>
<thead>
<tr>
<th>Star</th>
<th>$\lambda$ (Å)</th>
<th>Line</th>
<th>$W_r$ (mÅ)</th>
<th>$v_{\text{LSR}}$ (km s$^{-1}$)</th>
<th>$f$</th>
<th>$N_{\text{A}}$(OH) (10$^{13}$ cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$ Per</td>
<td>3078.4530</td>
<td>$Q_{11}(3/2) + Q_{21}(3/2)$</td>
<td>3.5 ± 0.7$^b$</td>
<td>10.8$^a$</td>
<td>1.04 × 10$^{-3}$</td>
<td>4.2 ± 0.7</td>
</tr>
<tr>
<td>$\zeta$ Per</td>
<td>3081.6645</td>
<td>$P_{11}(3/2)$</td>
<td>$\leq 2.1$</td>
<td>...</td>
<td>6.42 × 10$^{-4}$</td>
<td>$\leq 4.0$</td>
</tr>
<tr>
<td>$\zeta$ Per</td>
<td>3078.4530</td>
<td>$Q_{11}(3/2) + Q_{21}(3/2)$</td>
<td>1.5 ± 0.3$^d$</td>
<td>10.5$^a$</td>
<td>1.04 × 10$^{-3}$</td>
<td>1.9 ± 0.2</td>
</tr>
<tr>
<td>$\zeta$ Per</td>
<td>3081.6645</td>
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<td>$\leq 1.8$</td>
<td>...</td>
<td>6.42 × 10$^{-4}$</td>
<td>$\leq 3.4$</td>
</tr>
</tbody>
</table>

$^a$ Wavelengths from Stark, Brault, & Abrams 1994. For the blend $Q_{11}(3/2) + Q_{21}(3/2)$, the listed wavelength is a weighted mean based on a ratio of line strengths 1.00:0.69.

$^b$ Crutcher & Watson 1976a.

$^c$ Federman 1982 obtained $v_{\text{LSR}}$(CH) $\sim$ 8 km s$^{-1}$ toward $\alpha$ and $\zeta$ Per.

$^d$ Chaffee & Lutz 1977 found 1.6 ± 0.2 and 1.1 ± 0.2 mÅ for $\lambda 3078$, 3081.
Involves

\[ H^+ \rightarrow O^+ \rightarrow OH^+ \rightarrow H_2O^+ \rightarrow H_3O^+ \rightarrow OH, \]

where \( H^+ \) arises from ionization by cosmic rays, \( O^+ \) from charge exchange, \( OH^+ \) from hydrogen abstraction, and \( OH \) from dissociative recombination. A significant fraction of the \( OH \) comes from the dissociative recombination of \( H_2O^+ \). The channel initiated by the reaction \( H_3O^+ + O \) is not considered because recent observations indicate that \( OH \) exists primarily in the vicinity of the \( H_2O^+ \) transition in envelopes where the abundance of \( H_3O^+ \) is greater than that of \( H_2O^+ \) (Wannier et al. 1993).

The chemical networks for HD and NH proceed via analogous mechanisms. The scheme for HD was described previously by Black & Dalgarno (1973), O'Donnell & Watson (1974), and Heiles, McCullough, & Glassgold (1993). It involves the sequence

\[ H^+ \rightarrow D^+ \rightarrow HD. \]

Here \( D^+ \) and HD are produced via charge exchange and isotope exchange. The ion-molecule production of NH is based on the sequence

\[ N^+ \rightarrow NH^+ \rightarrow NH_2^+ \rightarrow NH_3^+ \rightarrow NH. \]

This scheme is initiated via ionization of atomic nitrogen by cosmic rays, followed by hydrogen abstraction reactions that form the \( NH_2^+ \) ions and dissociative recombination that yields NH. The scheme differs from that utilized by van Dishoeck & Black (1986), where the reaction \( H_3O^+ + N \) initiated the sequence. This reaction, however, is probably not effective (Huntress 1977; Herbst, DeFrees, & McLean 1987). Furthermore, production of the terminal ion \( NH_2^+ \) via hydrogen abstraction does not compete with dissociative recombination of \( NH_2^+ \), a consequence of its being a thermonuclear reaction (see references in Anichich 1993). Dissociative recombination of both \( NH_2^+ \) and \( NH_3^+ \) produces NH.

Steady state chemical rate equations, where production terms are set equal to destruction terms, are used here. The simplification of steady state is a reasonable one for cloud envelopes because chemical timescales tend to be the shortest. The rate equations for each species involved in the chemistries of OH, HD, and NH appear in Appendix A. In what follows, \( x(X) \) and \( N(X) \) are the fractional abundance relative to total number of protons and column density for species \( X \), respectively, \( k_i \) is the rate constant for reaction \( i \), \( \alpha(He^+) \) is the radiation recombination coefficient for \( He^+ \), and \( G(X) \) is the photodissociation rate for molecule \( X \). Furthermore, the total gas density \( n \) equals \( n(H) + 2n(H_2) \) and the optical depth at ultraviolet wavelengths (1000 Å) due to grain absorption and scattering is \( \tau_{uv} \). Although the derived column densities do not include the effects of variations with depth into a cloud, our previous work (e.g., Federman et al. 1994) indicates that this simplification provides results consistent with more detailed analyses. Our analysis uses these rate equations in order to extract the cosmic-ray ionization rate, the elemental abundance of deuterium, and the source for NH production (gas phase vs. another). The primary cosmic-ray ionization rate \( \zeta_p \) is obtained by inverting the expression for the column density of OH (eq. [A7]):

\[ \zeta_p = 0.4 \zeta_{H}/x(H), \] (1)

where

\[ \zeta_{H} = \frac{N(OH)}{0.8k_{i}N(O)} \left[ 2\alpha(He^+)x(e) + k_1 x(O) \right] \times \left[ k_3 x(C^+)n + G(OH) \exp \left(-\tau_{uv} \right) \right]. \] (2)

The elemental abundance of D is obtained by inverting equation (A10) for \( N(HD) \), namely,

\[ \zeta(D) = \frac{0.5N(HD)}{k_{i}k_{v}N(H_2)} \left[ 2\alpha(He^+)x(e) + k_1 x(O) \right] \times \left[ k_3 x(H) + k_4 x(H_2) \right] G(HD) \exp \left(-\tau_{uv} \right). \] (3)

The feasibility of producing the observed \( N(NH) \) toward \( \zeta \) Per (Meyer & Roth 1991) via gas-phase processes initiated by cosmic-ray ionization is studied with equation (A16). It is also used to make predictions regarding \( N(NH) \) toward the other two stars in our study, \( o \) Per and \( \xi \) Per. The expression is rewritten here for completeness:

\[ N(NH) \approx 0.5z_{N}N(N) \frac{G(NH) \exp \left(-\tau_{uv} \right)}{G(HD) \exp \left(-\tau_{uv} \right)}. \] (4)

The values for the rate constants and rates utilized in our analysis appear in Table 2. The pertinent reaction, the associated parameter for the rate constant/rate, its value, and the reference for the value are indicated. Although HD, like \( H_2 \), is destroyed through absorption of ultraviolet radiation in lines, a consideration of radiative transfer in the lines is not necessary as long as the lines of HD, unlike the \( H_2 \) lines, are always relatively optically thin to dissociating radiation. The analysis presented by Heiles et al. (1993), but for conditions appropriate to our sight lines, indicates that this assumption is valid for HD. Use of Draine's (1978) radiation field would raise our value for \( G(HD) \) by some 20%-30%, but the onset of self-shielding would compensate for this increase. Therefore, in our analysis only grain attenuation is incorporated when describing the photodissociation rate for HD.

In order to proceed, the column densities for \( O, OH, HD, H_2 \), and \( N \) are required, as are the fractional abundances for \( C^+ \) and \( O \). These are available from various sources, but the measured equivalent widths were used to rederive column densities either when new oscillator strengths were appropriated or when diverse sources for a given species were utilized. The column density for \( H_2 \) and the column density for total protons, \( N(H) + 2N(H_2) \), which is needed for fractional abundances of \( C^+ \) and \( O \), were taken from Savage et al. (1977). Through the use of \( f \)-values calculated by Allison & Dalgarno (1970), the HD column densities were derived from equivalent widths presented by Snow (1975) for \( o \) Per, Snow (1977) for \( \xi \) Per, and Spitzer, Cochran, & Hirshfeld (1974) for \( \zeta \) Per. For \( o \) Per, two lines of greatly differing strengths provided a reliable estimate for the Doppler parameter of 2.1 km s\(^{-1}\), which is consistent with results from high-resolution spectroscopy of CH absorption (Federman 1982; Crane et al. 1995). For the other sight lines, the \( h \)-values from the high-resolution studies were adopted—2.0 and 3.0 km s\(^{-1}\), respectively, for \( \zeta \) and \( \xi \) Per. For comparison, our column densities are similar to the ones quoted in the original references and are within 15% of the ones quoted by van Dishoeck & Black (1986). The values for \( N(OH) \) are from the present work.

Recent results from the Hubble Space Telescope (HST) were adopted for atomic column densities whenever possible.
TABLE 2

RATE CONSTANTS AND RATES

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺ + O → O⁻ + H</td>
<td>k₁</td>
<td>6.4 x 10⁻¹⁰e⁻²³²₃/T cm³ s⁻¹</td>
</tr>
<tr>
<td>C⁺ + O → CO⁺ + H</td>
<td>k₂</td>
<td>5.4 x 10⁻⁹ cm⁻³ s⁻¹</td>
</tr>
<tr>
<td>H⁺ + D⁺ + H</td>
<td>k₃</td>
<td>1.0 x 10⁻⁹ cm⁻³ s⁻¹</td>
</tr>
<tr>
<td>D⁺ + H → H⁺ + D⁺</td>
<td>k₄</td>
<td>1.0 x 10⁻⁹ cm⁻³ s⁻¹</td>
</tr>
<tr>
<td>D⁺ + HD → HD⁺ + H⁺</td>
<td>k₅</td>
<td>1.4 x 10⁻⁹ cm⁻³ s⁻¹</td>
</tr>
<tr>
<td>He⁺ + e⁻ → He + hv</td>
<td>a(He⁺)</td>
<td>4.2 x 10⁻¹⁰ cm⁻³ s⁻¹</td>
</tr>
<tr>
<td>OH + hv → O + H</td>
<td>G(OH)</td>
<td>1.0 x 10⁻⁹ cm⁻³ s⁻¹</td>
</tr>
<tr>
<td>HD + hv → H + D (ν = 1)</td>
<td>G(D)</td>
<td>5.0 x 10⁻¹⁰ cm⁻³ s⁻¹</td>
</tr>
<tr>
<td>NH + hv → N + H</td>
<td>G(NH)</td>
<td>2.3 x 10⁻¹⁰ cm⁻³ s⁻¹</td>
</tr>
<tr>
<td>p + H → H⁺ + e⁻ + p</td>
<td>ζ₁</td>
<td>1.5ζₓ</td>
</tr>
<tr>
<td>p + H → H⁺ + e⁻ + p</td>
<td>ζ₂</td>
<td>2.3ζₓ</td>
</tr>
</tbody>
</table>

* Péquignot et al. fitted their calculated radiative recombination coefficients with the function [8.295 × 10⁻¹³(T/10⁵)⁻⁰.₆₅⁰⁶³] × [1 + 0.9164(T/10⁵)⁰.₂₆₆⁷³] cm³ s⁻¹.


TABLE 3

MODELING PARAMETERS AND RESULTS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>o Per</th>
<th>ζ Per</th>
<th>ξ Per</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>N(OH) (cm⁻²)</td>
<td>8.2(13)</td>
<td>4.2(13)</td>
<td>≤4.2(13)</td>
</tr>
<tr>
<td>N(O) (cm⁻²)</td>
<td>7.4(17)</td>
<td>4.8(17)</td>
<td>6.0(17)</td>
</tr>
<tr>
<td>N(HD) (cm⁻²)</td>
<td>5.4(15)</td>
<td>3.2(15)</td>
<td>3.8(14)</td>
</tr>
<tr>
<td>N(H₂) (cm⁻²)</td>
<td>4.1(20)</td>
<td>4.7(20)</td>
<td>3.4(20)</td>
</tr>
<tr>
<td>N(N) (cm⁻²)</td>
<td>1.9(17)</td>
<td>1.6(17)</td>
<td>1.6(17)</td>
</tr>
<tr>
<td>x(O)</td>
<td>4.6(4)</td>
<td>3.0(4)</td>
<td>3.0(4)</td>
</tr>
<tr>
<td>x(C⁺)</td>
<td>2(4)</td>
<td>1.1(4)</td>
<td>2.5(4)</td>
</tr>
<tr>
<td>x(ς = 1.5x(C⁺))</td>
<td>3(4)</td>
<td>1.7(4)</td>
<td>3.8(4)</td>
</tr>
<tr>
<td>x(H)</td>
<td>0.44</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td>x(H₂)</td>
<td>0.22</td>
<td>0.22</td>
<td>0.22</td>
</tr>
<tr>
<td>n (cm⁻³)</td>
<td>400</td>
<td>350</td>
<td>150</td>
</tr>
<tr>
<td>Tₚ (K)</td>
<td>48</td>
<td>57</td>
<td>61</td>
</tr>
<tr>
<td>τ[op]</td>
<td>1.3(16)</td>
<td>1.7(17)</td>
<td>≤2.6(17)</td>
</tr>
<tr>
<td>I[op]</td>
<td>1.0</td>
<td>1.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Results</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ζ (s⁻¹)</td>
<td>1.2(16)</td>
<td>1.7(17)</td>
<td>≤2.6(17)</td>
</tr>
<tr>
<td>θ(D)</td>
<td>9.6(6)</td>
<td>1.9(5)</td>
<td>≥1.0(5)</td>
</tr>
<tr>
<td>N(NH) (cm⁻²)</td>
<td>7.6(11)</td>
<td>1.0(11)</td>
<td>≤5.7(10)</td>
</tr>
</tbody>
</table>

* Numbers in parentheses denote powers of 10.

** Estimate.

1994. As stated above, τ[op] is the optical depth due to grain absorption and scattering at ultraviolet wavelengths; I[op] indicates the strength of the local ultraviolet radiation field relative to the average interstellar field as described by Draine (1978). The fractional abundances for H and H₂ are based on the assumption that equal numbers of protons come from the two species. This assumption is consistent with the results of Wannier et al. (1993), who obtained strip maps of OH emission across cloud envelopes; they concluded that most of the OH resides near the H-to-H₂ transition. The kinetic temperature is assumed to equal the rotational temperature for H₂ deduced by Savage et al. (1977). The H₂ rotational temperature is used for the kinetic temperature in the present analysis because the species considered here are more widely distributed along the line of sight than are C₂ and CN. For the same reason, a value of n half that in Federman et al. (1994) is adopted, consistent with their findings for the gas toward ζ Oph.

The results from the analysis for each sight line appear at the bottom of Table 3. The primary cosmic-ray ionization rate, the elemental abundance of D, and the estimate for N(NH) from gas-phase processes (eq. [4]) are listed. The results for ζ Per toward ζ Per are similar to values expected in the interstellar medium from extrapolations of the measured flux at Earth of higher energy cosmic rays, ~10⁻¹⁷ s⁻¹ (Spitzer & Tomasko 1968), while the rate is some 5-10 times greater toward o Per. Similar differences were found previously by Hartquist et al. (1978) and van Dishoeck & Black (1986). The derived elemental abundance for D is within ~30% of the average value deduced for the atomic D/H ratio from Lyman lines by McCullough (1992)—namely, (1.5 ± 0.2) x 10⁻⁵—and more recently from HST spectra by Linsky et al. (1993)—1.65 ± 0.07 x 10⁻⁵. The column density of NH toward ζ Per predicted by our gas-phase analysis is significantly below the observed value of 9 x 10¹¹ cm⁻² (Meyer & Roth 1991), suggesting that another process produces most of the observed NH (see also Wagenblast et al. 1993). Our predicted value for N(NH), however, is comparable to the measured upper limit toward o Per (Crutcher & Watson 1976b). The much larger cosmic-ray ionization rate found by us toward o Per clearly is the reason for the closer correspondence. The next section provides a more thorough comparison with available modeling efforts.
4. DISCUSSION

4.1. Comparison of Modeling Efforts

Most chemical studies yield cosmic-ray ionization rates in the range \( \sim 10^{-12} \) to \( \sim 10^{-16} \) s\(^{-1}\). The differences found between studies for a given line of sight usually result from applying different assumptions to the models. For instance, since photodissociation is so important in cloud envelopes, the value for \( I_{\text{UV}} \) used in a calculation manifests itself in the value derived for \( \zeta_p \). Another example relates to estimates of \( \zeta_p \) from HD chemistry. These estimates are sensitive to the value used for the elemental abundance of D. Consideration of production mechanisms other than the gas-phase ones described here tends to lower the estimates of the ionization rate. Models incorporating shocks that produce OH through the reaction \( O + H_2 \rightarrow OH + H - \Delta E \) rely less on cosmic-ray ionization. Thus, care has to be taken when comparing the results from different studies.

First, we compare our results and those of Hartquist et al. (1978) and those of van Dishoeck & Black (1986) because all three studies are based on similar chemical schemes. These studies are in agreement in that the estimates of \( \zeta_p \) toward \( o \) Per are several times larger than the estimates toward \( \xi \) Per. This is mainly a consequence of the fact that the assumed \( T \) is lower and the value for \( x(C^+) \) is larger toward \( o \) Per; it is not caused by the larger value for \( N(OH) \), because the ratio \( N(OH)/N(O) \) is comparable for the two sight lines. With reference to equation (2), the lower \( T \) leads to a factor of 2 decrease in \( k_1 \) in the denominator while the larger abundance enhances the numerator. Moreover, the present values for \( \zeta_p \) are quite similar to those of Hartquist et al. (1978). The relatively slight differences (less than a factor of 2) arise from the values utilized by Hartquist et al. for \( N(OH) \) toward \( o \) and \( \xi \) Per and \( \xi(D) \) toward \( \xi \) Per. Such previous results relied on observed values for \( N(OH) \) that were larger than our values because they were based on smaller \( f \)-values.

Our estimates of \( \zeta_p \) tend to be smaller than the estimates of van Dishoeck & Black (1986). This is primarily caused by the larger ultraviolet fluxes adopted in their models. They considered larger fluxes in order to explain the observed distribution of \( H_2 \) rotational levels; however, other means of populating the excited rotational levels, such as during formation on grains and the presence of warm gas, are available. This indeed is found to be the case for the gas toward \( \zeta \) Oph, where less \textit{vibrationally} excited \( H_2 \) is observed than predicted by their models based solely on photon pumping (Federman et al. 1995).

The chemical model of Heck et al. (1993) for the direction toward \( o \) Per includes the presence of a magnetohydrodynamic shock, mainly for the purpose of attempting to reproduce the observed amount of \( CH^+ \) and several high-lying \( H_2 \) rotational levels. Their modeling effort was quite successful in this regard. Of note for our discussion, the calculated distribution of \( H_2 \) rotational levels agrees better with observations than the results presented by van Dishoeck & Black (1986), especially for \( J = 3 \) and 4. Since Heck et al. used a value for \( I_{\text{UV}} \) of 1, that is, no enhancement in the flux over the interstellar value, the warm shocked gas is needed to account for the observed rotational populations.

A substantial amount of OH (nearly 30\%) is produced via the reaction \( O + H_2 \) within the shocked gas in the models of Heck et al. (1993). This explains why they required a lower cosmic-ray ionization rate than we do—\( 5.5 \times 10^{-17} \) s\(^{-1}\) versus \( 1.3 \times 10^{-16} \) s\(^{-1}\). Both estimates for \( \zeta_p \) could be lowered a bit more since our OH data, in particular the upper limit for the line at 3081 Å, suggest that \( N(OH) \) is lower than Heck et al.'s adopted column density. Use of a smaller ionization rate would also lower our predicted value for \( N(NH) \), which is similar to the upper limit found by Crutcher & Watson (1976b). The same applies to the model predictions presented by van Dishoeck & Black (1986). One question that remains to be answered in the picture of Heck et al., however, involves the lack of OH toward \( \xi \) Per, although the observed column density of \( CH^+ \) is approximately twice as large toward this star—i.e., since a shock is expected to produce both OH and \( CH^+ \), where is the OH associated with the \( CH^+ \) toward \( \xi \) Per?

Even with such reductions, \( \zeta_p \) is larger toward \( o \) Per than toward the other two directions in our study. Of the three lines of sight, \( o \) Per is closest to the star-forming region associated with IC 348. It is possible that the enhanced flux of cosmic rays arises from the presence of young, massive stars. This suggestion is reminiscent of the recent finding by Bloemen et al. (1994) of enhanced flux of heavy cosmic rays in the vicinity of the Orion Nebula.

Wagenblast et al. (1993) presented a time-dependent chemical study of the line of sight to \( \xi \) Per that included molecular formation on grain surfaces. In this model, rotationally excited \( H_2 \) occurs during formation on grains, not through photon pumping or shocks. In order to minimize the contribution from photon pumping to the excitation process, they used a very low ultraviolet flux (i.e., \( I_{\text{UV}} \ll 1 \)). Although their photodissociation rates are much less than ours, both modeling efforts suggest similar values for \( \zeta_p \). This is partly the result of the fact that, even in our models, most of the destruction of OH arises from the reaction \( C^+ + OH \). The agreement is somewhat superficial, however, because many of the other input parameters differ in the two models. Substantially different values for \( N(O) \) (50\%), \( n \) (a factor of 3), and \( \xi(D) \) (a factor of several) were utilized. A particularly pleasing result of their analysis is its ability to reproduce the value of \( N(NH) \) measured by Meyer & Roth (1991) through incorporation of nitrogen hydride (\( NH_n, n = 1-3 \)) production on grain surfaces with an efficiency \( \sim 30\% \) of that for \( H_2 \) formation. Ion-molecule (gas phase) schemes (van Dishoeck & Black 1986; this paper) produce far too little NH toward \( \xi \) Per.

The above discussion highlights an important point. The differences \textit{and similarities} among modeling efforts arise from the assumptions that then lead to a specific set of input parameters used in the analyses. This diversity in input parameters can be restricted by two sources. First, more high-quality astronomical data, such as the recent measurements of atomic and molecular abundances made with \textit{HST} (e.g., Cardelli et al. 1991a and Meyer et al. 1995 for atoms and Federman et al. 1995 and Lambert, Sheffer, & Federman 1995 for molecules), are required. Second, laboratory data on important reactions still are lacking. Although recent theoretical calculations have provided much needed information on chemical rates and photodissociation, experimental verification is often desirable. An example involves the rate constant for the reaction \( C^+ + OH \). The recent calculation by Dubernet, Gargaud, & McCarroll (1992) is consistent with the earlier suggestion by Federman & Huntress (1989) that this reaction occurs at the collision rate. Since the reaction involves the radical
OH, it is a difficult one to study in the laboratory, but recent progress in laboratory techniques suggests that it can be done (V. G. Anicich 1993, private communication).

4.2. Correspondences

Published results on detections of OH absorption at ultraviolet wavelengths are limited to three sight lines, o Per, ζ Per, and ζ Oph (see Smith & Snow 1979 and above references for work prior to the present study). A reason for the limited success in detecting OH is suggested by our results for ζ Per. How does the line of sight toward ζ Per differ from those toward o Per, ζ Per, and ζ Oph from an observational perspective? Although the values for both N(H₂) and N(CH) are within a factor of 2 for these sight lines, N(CO) is more than a factor of 10 lower toward ζ Per. A comparison with CO is especially relevant because most of the CO production arises from the reaction C⁺ + OH. Since CO is easily detected via relatively strong ultraviolet transitions, future searches for OH absorption should focus on lines of sight with substantial columns of CO [N(CO) > 10¹⁵ cm⁻²]. The negative results on OH absorption toward α Cam and σ Sco (Smith & Snow 1979) are consistent with this premise.

The correspondence between detecting OH absorption and ζ Per is more subtle. The observed N(HD) is similar toward ζ Per and ζ Oph, yet OH is observed only toward ζ Oph in spectra with comparable signal-to-noise ratios (see Table I for ζ Per and Crutcher & Watson 1976a for ζ Oph—note that our data confirm their detection toward o Per). Federman et al. (1994) inferred that the ultraviolet flux permeating the gas toward ζ Per is greater than that toward o Per, ζ Per, and ζ Oph, in part because grain extinction is lower toward ζ Per. Then it is possible that the OH abundance toward ζ Per is lower because there is enhanced ultraviolet flux in this direction.

Meyer & Roth (1991) detected NH absorption toward ζ Per and HD 27778 (62 Tau); the amount of NH is 3 times greater toward HD 27778. This difference is not likely to be caused by an enhanced cosmic-ray ionization rate toward HD 27778. Instead, there is less photodissociation occurring in the sight line; Federman et al. (1994) suggested that an ultraviolet flux lower than is typical for interstellar space is needed to reproduce the observed N(CN).

Since our OH observations confirm the earlier results of Crutcher & Watson (1976a) and Chaffee & Lutz (1977), the combined results on λ3078 can be used to infer the f-value for the D – X (0, 0) transitions near 1222 Å. The observed equivalent widths for the $Q_{11}(3/2)$ line at 1222.071 Å for o Per (Snow 1975) and for ζ Per (Snow 1977), with a HönLondon factor of 0.56 for the line, indicate a band oscillator strength of 1.3 × 10⁻², which is in excellent agreement with the theoretical determination of 1.2 × 10⁻² by van Dishoeck, Langhoff, & Õgelman (1983). The slight difference between this result and the value derived by Chaffee & Lutz (1977) is caused by the adopted value for $f_{\text{mol}}(A-X)$. Further refinement in the astronomical derived value could easily be accomplished through HST observations with the Goddard High-Resolution Spectrograph. From observations with the Copernicus satellite, Snow (1975, 1977) obtained equivalent widths for the D – X line of 3 – 5 mÅ. Much weaker interstellar features are routinely measured from HST spectra at similar wavelengths (see, e.g., Cardelli, Savage, & Ebbets 1991b; Federman et al. 1995).

4.3. Concluding Remarks

New measurements of interstellar OH absorption at 3078 and 3081 Å, the first obtained with a CCD detector, have been presented. The observations were analyzed with the aid of a simple chemical model; the analysis provides estimates of the cosmic-ray ionization rate, $ζ_p$. The lack of OH absorption toward ζ Per is probably caused by an enhanced ultraviolet flux in this direction. Future searches for OH absorption are more likely to be successful if lines of sight rich in CO are considered.

Since our analysis is based on more secure atomic abundances from HST observations and more recent information on reaction rates than earlier studies, the limitations of such analyses are now more clearly defined. Comparisons with other modeling efforts show the emergence of some general trends, such as consistently inferring an enhanced cosmic-ray flux toward o Per, but the various assumptions affecting the input into the models do not yet lead to general consensus regarding the environments probed by these measurements. Additional observations and laboratory experiments are suggested.

Once $ζ_p$ was established, available observations of HD and NH were modeled. The HD observations yield an elemental abundance of deuterium that is consistent with the interstellar value found by McCullough (1992) and Linsky et al. (1993). This ability of the ion-molecule schemes indicates that these are indeed the primary routes for OH and HD production in cloud envelopes. As first suggested by Wagenblast et al. (1993) from detailed calculations, a source other than ion-molecule chemistry initiated by cosmic-ray ionization is needed to reproduce the observed column density of NH molecules.

We thank Dave Meyer for providing results before publication and the referee, John Black, for information about OH f-values. We also acknowledge helpful discussions with Dan Welty concerning interstellar Ti II. This work was supported in part by NASA grant NAGW-3840 (S. R. F.) and by the Robert A. Welch Foundation of Houston, Texas (D. L. L.). J. W. participated in the Research Experience for Undergraduates at the University of Toledo through funds provided by the National Science Foundation under grant PHY 92-00403.

APPENDIX A

ION-MOLECULE CHEMISTRY

This appendix contains the rate equations used to derive the expressions for the analysis described in the main text. Simplifications involve restricting the chemical schemes to the environment considered here, namely, cloud envelopes, and are based on recent compilations of rate constants (e.g., Anicich 1993 for ion-molecule reactions and Mitchell 1990 for dissociative recombination) and photodestruction rates (e.g., van Dishoeck 1987). In all cases, reactions that contribute less than
25% to a specific process are not included in our equations. The following steady state rate equations for each species are derived by setting production terms equal to destruction terms. In these equations, \( x(X) \) is the abundance of species \( X \) relative to the total number of protons, \( k_i \) are rate constants, \( G(X) \) and \( \beta(X) \) are photorates and recombination rate constants, respectively, for species \( X \), and \( \zeta \) are cosmic-ray ionization rates. The optical depth at 1000 Å due to grain absorption and scattering is given by \( \tau_{\text{UV}} \). For comparison with observations, column densities replace abundances in our rate equations. Although this approach does not provide information about variation as a function of depth in a cloud, our previous experience (e.g., Federman et al. 1994) and the analyses here show that this assumption yields results consistent with more detailed calculations, such as those of van Dishoeck & Black (1986).

The rate equations for the oxygen species are

\[
x(O^+) \approx \frac{k_1 x(H^+)x(O)}{k_2 x(H) + k_3 x(H_2)}, \quad x(OH^+) \approx \frac{k_3 x(H_2)x(O^+)}{k_4 x(H_2)}, \quad (A1)
\]

\[
x(H_2O^+) \approx \frac{k_4 x(H_2)x(OH^+)}{k_5 x(H_2) + \beta(H_2O^+)x(e)}, \quad x(H_3O^+) \approx \frac{k_2 x(H_2)x(H_2O^+)}{\beta(H_3O^+)x(e)}, \quad (A2)
\]

\[
x(OH) \approx \frac{(\beta(H_2O^+)x(H_2O^+) + \beta(H_3O^+)x(H_3O^+))x(e)n}{k_6 x(C^+)n + G(OH) \exp (-\tau_{\text{UV}})}, \quad (A3)
\]

where \( \beta \) represents the fraction of recombinations that lead to OH. Substitution of equations (A1)–(A2) into equation (A3) yields

\[
x(OH) \approx \frac{0.4k_1 x(H^+)x(O)n}{k_6 x(C^+)n + G(OH) \exp (-\tau_{\text{UV}})}, \quad (A4)
\]

which includes an approximation that the number of protons from H and H\(_2\) are equal—i.e., \( x(H) = 2x(H_2) \). The numerical factor arises because \( \left(1\right) \beta(H_2O^+) = \beta(H_2O^+) \) (Mitchell 1990; Mul et al. 1983), \( \left(2\right) \beta(H_3O^+) \approx \beta(H_3O^+) \) (Glassgold & Langer 1976), and \( \left(3\right) \beta(H_3O^+) = 0.65\beta(H_2O^+) \) (Herd, Adams, & Smith 1990). As a result of the small branching ratio for H\(_2\)O formation via H\(_3\)O\(^+\) + e and the fact that ions readily attack the dipolar H\(_2\)O, production of OH from the photodissociation of H\(_2\)O is not important. A simplified rate equation for \( x(H^+) \) based on that from Glassgold & Langer (1974) is

\[
x(H^+) \approx \frac{2\zeta_H}{2x(He^+)x(e)n + k_1 x(O)n}, \quad (A5)
\]

where \( \zeta(He^+) \) is the radiative recombination rate constant for He\(^+\) and \( \zeta_H \approx x(H)(\zeta_1 + 0.5\zeta_2) \approx 2.5\zeta_\rho x(H) \). The cosmic-ray ionization rates for H and H\(_2\), respectively, are \( \zeta_1 \) and \( \zeta_2 \), while \( \zeta_\rho \) is the primary cosmic-ray ionization rate. The final expression for OH then becomes

\[
x(OH) \approx \frac{0.8k_1 \zeta_H x(O)}{[2x(He^+)x(e) + k_1 x(O)] [k_6 x(C^+)n + G(OH) \exp (-\tau_{\text{UV}})]}, \quad (A6)
\]

or, in terms of column densities \( N(X) \),

\[
N(OH) \approx \frac{0.8k_1 \zeta_H N(O)}{[2x(He^+)x(e) + k_1 x(O)] [k_6 x(C^+)n + G(OH) \exp (-\tau_{\text{UV}})]}, \quad (A7)
\]

from which the primary cosmic-ray ionization rate can be obtained.

The appropriate rate equations for species related to HD formation are

\[
x(D^+) \approx \frac{k_7 x(D)x(H^+)}{k_8 x(H) + k_9 x(H_2)}, \quad x(HD) \approx \frac{k_9 x(H_2)x(D^+)n}{G(HD) \exp (-\tau_{\text{UV}})} \quad (A8)
\]

Since the relative abundance of atomic D, \( x(D) \), is equal to \( \zeta(D) - x(D^+) - x(HD) \), where \( \zeta(D) \) is the elemental abundance of deuterium, the equation for \( x(D) \) can be written

\[
x(D) = \zeta(D) \left\{ 1 + \frac{k_7 k_9 x(H^+)x(H_2)n}{[k_8 x(H) + k_9 x(H_2)] G(HD) \exp (-\tau_{\text{UV}})} \right\}^{-1}. \quad (A9)
\]

Upon substitution of \( x(D) \) and \( x(H^+) \), the equation for the abundance of HD becomes

\[
x(HD) = \frac{2k_7 k_9 \zeta_D x(H_2)}{[2x(He^+)x(e) + k_1 x(O)] [k_8 x(H) + k_9 x(H_2)] G(HD) \exp (-\tau_{\text{UV}})}. \quad (A10)
\]

The values for \( \zeta(D) \) are found by inverting the above expression and by using the observed quantities \( N(HD) \) and \( N(H_2) \) for \( x(HD) \) and \( x(H_2) \).

Finally, the rate equations for the nitrogen species are

\[
x(N^+) \approx \frac{\zeta_N x(N)}{k_{10} x(H_2)n}, \quad x(NH^+) \approx \frac{\zeta_N x(N)}{k_{11} x(H_2)n}. \quad (A11)
\]
\[ x(\text{NH}_2^+) \approx \frac{\zeta_N x(N)}{\beta(\text{NH}_2^+) x(e)n + k_{12} x(\text{H}_2)n} \tag{A12} \]

\[ x(\text{NH}_3^+) \approx \frac{k_{12} \zeta_N x(N) x(\text{H}_2)}{[\beta(\text{NH}_2^+) x(e) + k_{12} x(\text{H}_2)] \beta(\text{NH}_3^+) x(e)n} \tag{A13} \]

\[ x(\text{NH}) \approx \frac{\beta(\text{NH}_2^+) x(\text{NH}_2^+) + \beta(\text{NH}_3^+) x(\text{NH}_3^+) + \beta(\text{NH}_3^+) x(\text{NH}_3^+) x(e)n}{G(\text{NH}) \exp (-\tau_{\text{UV}})} \tag{A14} \]

The last term in the square brackets arises from NH production via the photodissociation of \( \text{NH}_2^+ \). After substituting the above expressions for \( x(\text{NH}_2^+) \) and \( x(\text{NH}_3^+) \) into the one for \( x(\text{NH}) \), and assuming that \( \beta(\text{NH}_2^+) \approx 0.5 \beta(\text{NH}_3^+) \), the equation for \( x(\text{NH}) \) is

\[ x(\text{NH}) \approx \frac{0.5 \zeta_N x(N)}{G(\text{NH}) \exp (-\tau_{\text{UV}})} \tag{A15} \]

or, in terms of column densities,

\[ \frac{N(\text{NH})}{N(N)} \approx \frac{x(\text{NH})}{x(N)} \approx \frac{0.5 \zeta_N}{G(\text{NH}) \exp (-\tau_{\text{UV}})} \tag{A16} \]

Our analysis of NH chemistry is not dependent on the rate constant \( k_{12} \) for the slightly endothermic reaction \( \text{N}^+ + \text{H}_2 \rightarrow \text{NH}^+ + \text{H} \), which is the principal destruction mechanism for \( \text{N}^+ \) and the principal production channel for \( \text{NH}^+ \), and therefore cancellation occurs in the steady state rate equations, as noted above.

**APPENDIX B**

**Ti II MEASUREMENTS**

Interstellar absorption from Ti II is usually studied through the line at 3383 Å (e.g., Stokes 1978; Albert 1982). The line at 3241 Å was detected toward ζ Per by Chaffee & Lutz (1977). To our knowledge, our detections of λ3072 are the first from a ground-based facility. The other two (weaker) transitions out of the ground state (λ3057, 3066) for the multiplet at 3079 Å fall beyond the spectral coverage of our measurements. The results from our observations are presented in Table 4, and the spectra appear in Figure 2. The table lists the line of sight, \( W_i \) with 1 \( \sigma \) uncertainties, and the derived column density based on an \( f \)-value of 0.109 (Morton 1991) and a \( b \)-value of 3 km s\(^{-1}\). The use of such a large \( b \)-value is the result of the association of Ti II absorption with the warm neutral medium (see Crinklaw, Federman, & Joseph 1994).

Our results yield column densities that are consistently 50% larger than those derived from values of \( W_{3383} \) obtained by Stokes (1978). The measurements of Magnani & Salzer (1991) for each star are consistent with Stokes's results. The equivalent width of Chaffee & Lutz (1977) for Ti II λ3383 is considerably smaller than the ones from the other studies and therefore would suggest an even larger discrepancy. (We note that our OH results and those of Chaffee & Lutz are in excellent agreement.)

D. Welty (1995, private communication) also finds a 50% difference when Stokes's results are compared with results from available data acquired with IUE. Scattered light should not greatly affect our determinations, because (1) multiple, adjacent orders were not imaged onto the CCD—i.e., a grating spectrometer, not an echelle spectrometer, was used—and (2) the use of two ultraviolet filters rejected stellar radiation present in first order. Finally, lowering the \( b \)-value to 1 km s\(^{-1}\), surely an extreme value, only increases the column densities from λ3383 by some 10%–20%.

The source of the discrepancy appears to be in the adopted oscillator strengths. Morton (1991) relied on the laser-excited lifetime measurements by Kwiatkowski, Werner, & Zimmerman (1985) for both multiplets' \( f \)-values. More recently, Bizzarri et al. (1993), who have redetermined \( f \)-values for 100 Ti II lines using newly measured radiative lifetimes and branching ratios, obtained \( f = 0.350 \pm 0.013 \) for the 3383 Å line. This more accurate value is consistent with that given by Morton (\( f = 0.340 \), with a 1 \( \sigma \) uncertainty of \( \sim 11\% \)). Bizzarri et al. did not quote an \( f \)-value for λ3072, but their measurements for other lines of the same multiplet indicate that Morton's adopted \( f \)-values are too small. The mean correction factor from four lines would yield \( f = 0.121 \) instead of Morton's \( f = 0.109 \), to which he assigned an uncertainty of \( \sim 9\% \). Since Bizzarri et al. provide a more accurate radiative lifetime for the upper state of the 3072 Å line (5% vs. 10%), the corrected \( f \)-value is likely to have a

<table>
<thead>
<tr>
<th>Star</th>
<th>( W_{3383} ) (mÅ)</th>
<th>( N ) (10(^{11}) cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>ζ Per</td>
<td>4.1 ± 1.0</td>
<td>4.6 ± 1.2</td>
</tr>
<tr>
<td>ζ Per</td>
<td>2.6 ± 0.6</td>
<td>2.9 ± 0.7</td>
</tr>
<tr>
<td>ζ Per</td>
<td>5.6 ± 1.0</td>
<td>6.4 ± 1.2</td>
</tr>
</tbody>
</table>
precision comparable to their result for λ3383 (≈ 5%), or \( f = 0.121 \pm 0.006 \).

The ratio of the equivalent widths is similar for the three stars, and the weighted mean for \( W_3/2.1 \pm 0.6 \) and \( 2.0 \pm 0.8 \) mA with respective LSR velocities of +9.2 and –3.9 km s\(^{-1}\). These components probably correspond to the strongest components A and Z found by Stokes (1978). For ζ Per, the values of \( W_r \) are 3.5 \pm 0.7 and 2.1 \pm 0.7 mA for the components at +9.9 and –6.3 km s\(^{-1}\). The +9.9 km s\(^{-1}\) feature is likely a combination of Stokes’s components A2–A4, while the negative-velocity component found here may be associated with his component A1. (Note that his Table 3 incorrectly identifies ζ Per as ζ Per on p. 124.) The narrower feature toward ζ Per seen in our spectrum is consistent with the dominant component A detected by Stokes. The discrepancy in derived column densities noted above is not altered by the presence of component structure because all the measured lines are relatively weak. A component-by-component comparison, however, is not possible because Stokes (1978) and Magnani & Salzer (1991) only provided total equivalent widths for each sight line.

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