Energy absorption by N_2O in the 4 to 14 eV region[*]

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Apparent oscillator-strength values for transitions in the 4 to 14 eV region in nitrous oxide have been derived from electron energy-loss measurements. Detailed comparison with photoabsorption measurements in the ultraviolet region indicates a weak transition below the $^1\Delta \leftarrow \tilde{X}\,^1\Sigma^+$ transition at 6.8 eV not observed optically. This analysis also provides oscillator-strength values in the region between 11.5 and 12.4 eV, where no quantitative photoabsorption data are available.

INTRODUCTION

Renewed interest in the energy-absorbing properties of nitrous oxide has been stimulated by recent concern over the possible depletion of the ozone layer. Since photodissociation of N_2O is the major natural source of nitric oxides that limit present ozone concentrations in the stratosphere,[1] it is an important component in any detailed analysis of this problem. But from a broader point of view, the energy-absorption properties (i.e., the oscillator-strength distribution) of N_2O is of fundamental importance to the analysis of any problem where energetic radiations encounter N_2O. In this regard, it is important to note that N_2O is widely used as an electron scavenger in radiation chemistry.

Although there have been several electron energy-loss studies[2-5] of nitrous oxide, very little oscillator-strength information has been extracted from these measurements. The electron energy-loss data of Weiss *et al.*[3] were used to obtain f values for seven Rydberg transitions, but their analysis did not extend to transitions below 13.5 eV. No other electron-impact work has been used to derive oscillator strengths for this molecule.

Absorption cross-section measurements on N_2O in the ultraviolet region have been reviewed by Hudson.[6] Other measurements of photoabsorption below 10 eV have subsequently been reported by Rabalais *et al.*[7] However, no single optical study has covered the entire region from 4 to 15 eV, and it has been pointed out to us recently[8] that no optical values are available in the small region between 11.8 and 12.4 eV. In previous work we have successfully derived oscillator-strength distributions for a number of molecules[9-11] from high-quality electron energy-loss spectra. These spectra have been obtained for 100 eV electrons scattered within 20 mrad of the incident direction. The same analysis has been carried out in this study of energy absorption by N_2O.

EXPERIMENTAL

The NBS model AN-1 electron-impact spectrometer used in this study is described elsewhere.[12] Digital energy-loss spectra of N_2O were obtained in the same manner as described previously for acetone[10] and oxygen.[11] These data were adjusted by calibration of the energy-loss scale to the position of the $2^1P \leftarrow 1^1S$ transition in helium and by a deadtime correction, as discussed previously.[11] Nitrous oxide prepared by Matheson with a stated purity of better than 98% was used without further purification. However, characteristic energy-loss peaks of possible common impurities, such as N_2, NO, O_2, and H_2O, were not seen in any of the spectral data analyzed in this work.

The apparent oscillator-strength distribution for N_2O shown in Fig. 1 was derived from electron energy-loss data. Our energy-loss spectrum was very nearly identical to that published by Weiss *et al.*[3] for an incident energy of 115 eV, although our energy resolution of 42 meV was somewhat worse than theirs. The data were corrected for the finite acceptance angle of the apparatus (e.g., $\hat{\theta} = 0.020$ rad) by the procedure detailed previously.[10,11] The relative oscillator-strength distribution was normalized at 13.41 eV in the ionization continuum region. A differential oscillator strength, $df/dE = 0.169\ \mathrm{eV}^{-1}$, was taken from the photoabsorption measurements of Cook, Metzger, and Ogawa.[13] This is the same normalization value as used by Weiss *et al.*[3] to derive f values for Rydberg transitions at higher energies.

DISCUSSION

The region below 10 eV is composed of three rather broad absorption bands with maxima at 6.83, 8.52, and 9.64 eV. Chutjian and Segal[14] have reviewed available experimental data in this region and proposed theoretical assignments for each of these bands. Unfortunately, very recent *ab initio* HF-SCF-CI calculations[15] now indicate that certain of these proposed assignments[14] are likely to be in error. Since complete discussions of these new theoretical results are in press, we will simply adopt the more recent assignments here (see Table I) without further critical comment.

In Table I we compare our integrated f values for those bands between the energy limits indicated with those derived from optical measurements.[7,16] The f value we obtain for the 6.83 eV transition is in close agreement with optical determinations, and is identified as the $\tilde{A}^1\Delta \leftarrow \tilde{X}^1\Sigma^+$ transition.[7,15] However, our differential oscillator-strength values below about 5.6 eV fall off more gradually than the optical data, as shown

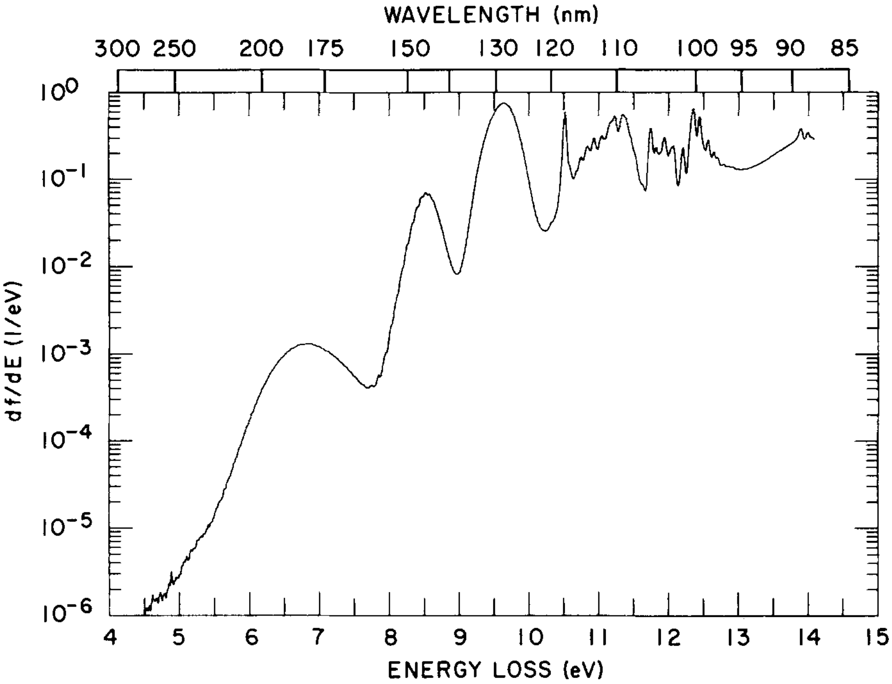

FIG. 1. Apparent oscillator-strength distribution for nitrous oxide derived from energy-loss measurements for 100 eV incident electrons.

in Fig. 2. The photoabsorption data (not shown) of Thompson, Harteck, and Reeves[17] also yields *df/dE* values less than 10^{-6} eV^{-1} at energies below about 5.4 eV. Although the total oscillator strength indicated by the electron-impact measurements between 4.5 and 5.6 eV is small (e.g., about 5×10^{-6}), it is definitely greater than that observed optically. It is possible that a temperature dependence effect similar to that reported by Holliday and Reuben[18] might be responsible for the broadening of the $\tilde{A}\,^1\Delta \leftarrow \tilde{X}\,^1\Sigma^+$ band observed for small energy losses. This could result from heating of the collision cell walls by the electron beam. However, direct comparison of our results with optical measurements at different fixed temperatures[18] shows a more gradual decline in intensity with decreasing energy. Specifically, our values separate from the optical measurements[18] at 20° C, cross the 100° C curve twice, and display a different spectral shape.

Recently, Hall, Chutjian, and Trajmar[5] have observed a new energy-absorption process in N_2O between 5 and 6 eV. They observed two important characteristics of this transition: (1) The intensity falls off upon increasing the incident energy above threshold, and (2) the intensity falls off with increasing scattering angle. These characteristics were taken as indicative of a multiplicity-allowed rather than spin-forbidden transition. Although Hall *et al.*[5] tentatively assigned this new band as $^1\Delta \leftarrow \tilde{X}\,^1\Sigma^+$ in accord with prior analysis,[14] such an assignment is inconsistent with recent theoretical calculations.[15] The only transition predicted[15] to occur below the $^1\Delta \leftarrow \tilde{X}\,^1\Sigma^+$ transition (6.8 eV), that is not multiplicity forbidden, is the $^1\Sigma^- \leftarrow \tilde{X}\,^1\Sigma^+$ at 6.5 eV. However, theory[15] places this transition at an energy too high to explain either the observations of Hall *et al.*[5] or the differences we observed from the optical data in the region near 6 eV. Although a fully satisfying explanation is lacking, it is possible that excitation of low-lying triplet states may be involved.[15]

TABLE I. Comparison of oscillator strengths for N_2O bands below 10 eV.

	Band energy limits[b]		Absorption *f* value	
Transition[a]	E_1 (eV)	E_2 (eV)	Electron impact	Photoabsorption
Unassigned	4.50	5.60	5.06×10^{-6}	$\sim2\times10^{-7}$ [c]
$\tilde{A}\,^1\Delta \leftarrow \tilde{X}\,^1\Sigma^+$	5.60	7.70	1.44×10^{-3}	1.5×10^{-3} [d] 1.4×10^{-3} [c]
$\tilde{B}\,^1\Pi \leftarrow \tilde{X}\,^1\Sigma^+$	7.70	8.97	2.85×10^{-2}	2.11×10^{-2} [d]
				7.20×10^{-3} [c]
$\tilde{C}\,^1\Sigma^+ \leftarrow \tilde{X}\,^1\Sigma^+$	8.97	10.23	0.352	0.367[d]
				0.36[c]

[a] State designations given in $C_{\infty v}$ Point Group representation.

[b] Vertical energy limits used in evaluating oscillator strengths from the electron energy-loss measurements.

[c] Reference 7.

[d] Reference 16.

For the band centered at 8.52 eV we obtain an *f* value (Table I) that is larger than optical determinations. It has been assigned[7] as the $\tilde{B}\,^1\Pi \leftarrow \tilde{X}\,^1\Sigma^+$ transition in accord with recent theoretical interpretations.[15] This band is composed of a continuum with superimposed diffuse vibrational bands (see Fig. 2). The large discrepancy between the two optically determined *f* values for this band, although these studies are in good agreement for the *f* values of neighboring bands, is indicative of line saturation problems in the optical measurements resulting in an underestimation of the actual oscillator strength for this band. Since electron-impact results are free of line saturation problems,[11] our value should be considered more reliable.

The dominant absorption process in the N_2O spectrum is the continuum band with a maximum at 9.64 eV. Our data indicate only a smooth continuum in this region in agreement with most other workers.[2-7] Our data

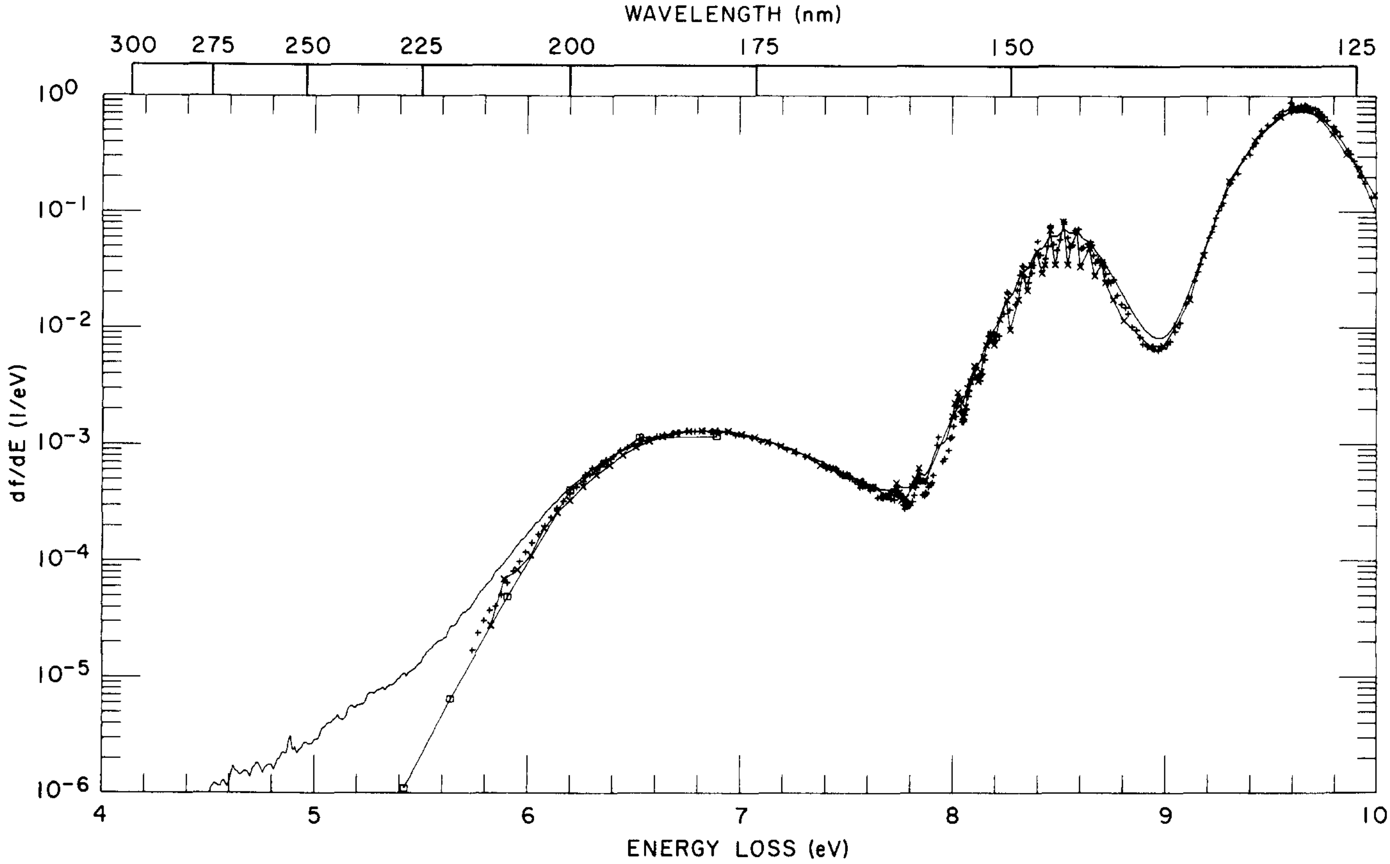

FIG. 2. Comparison of optical and electron-impact oscillator strengths in the 4–10 eV region: +, Ref. 16, ×, Ref. 7; □ Ref. 1; solid line, present results.

do not show any indication of the sharply peaked structure in this region, as reported by Zelikoff *et al.*[16] Recent photolysis experiments[19] indicate absorption in this region leads to dissociation into $N_2(\tilde{X}^1\Sigma_g^+) + O(^1S)$ with a quantum yield of unity at 129 nm. These dissociation products are consistent with assignment this transition as $\tilde{C}^1\Sigma^+ \leftarrow \tilde{X}^1\Sigma^+$. Our integrated f value for this band agrees closely with optical determinations (see Table I). However, all experimental values are about one-half of the theoretical value[14] obtained for the $\tilde{C}^1\Sigma^+$ transition. Although this discrepancy is not excessive, it may be due to the limited basis set used by Chutjian and Segal,[14] which was chosen to yield best results for states with greatest valence character. However, the energy of this band coincides with the calculated position[20] of the $n = 3$ member of the $ns\sigma$ Rydberg series converging to the lowest ionization potential. Thus, it is possible that the intensity of the $\tilde{C}^1\Sigma^+ \leftarrow \tilde{X}^1\Sigma^+$ transition is influenced by some unaccounted for interaction with the $3s\sigma$ Rydberg state.

The energy-absorption region between 10 and 14 eV is shown in greater detail in Fig. 3 on a linear scale Here the oscillator-strength distribution derived from the energy-loss data is compared with the optical measurements of Zelikoff *et al.*[16] (10 to 11.5 eV) and by Cook *et al.*[13] (12.4 to 14.0 eV). No optical values are available for comparison in the region between 11.5 and 12.4 eV. The agreement in intensity with Zelikoff *et al.*[16] is good when one allows for the better resolution obtained in their work. However, above 10.8 eV the centers of their absorption maxima appear to be displaced to higher energies by about 30 meV (i.e., a shift of approximately 0.3 nm to shorter wavelengths). As can be seen in Fig. 3, the peak positions observed in the present work are in better agreement with the strong diffuse progression (indicated by vertical lines above the spectrum) observed in the high-resolution work of Tanaka *et al.*[21]

No quantitative photoabsorption data are available for comparison with the present results in the region between 11.5 and 12.4 eV. Our results show an apparent absorption window located at 11.67 eV (~ 106.2 nm) followed by at least six well-defined peaks at 11.75, 11.83, 11.95, 12.07, 12.21, and 12.36 eV. The sharp peaks at 10.52, 11.75, and 12.07 eV are the first three members of a Rydberg series converging to the $\tilde{X}^2\Pi$ ion state (12.9 eV) as first identified by Tanaka *et al.*[21] Recent calculations[20] indicate that the $n = 3$, 4, and 5 term values for the $np\sigma$ and $np\pi$ Rydberg orbitals correlate closely with these structures. Members of this series with $n > 5$ are evident in the structure observed above 12.4 eV. However, the intensities for transitions to these higher Rydberg orbitals appear to be strongly enhanced by the opening of a new channel of excitation,[22] namely, excitation of the $3s\sigma$-Rydberg state (12.36 eV) associated with the $^2\Sigma^+$ ion core. Such

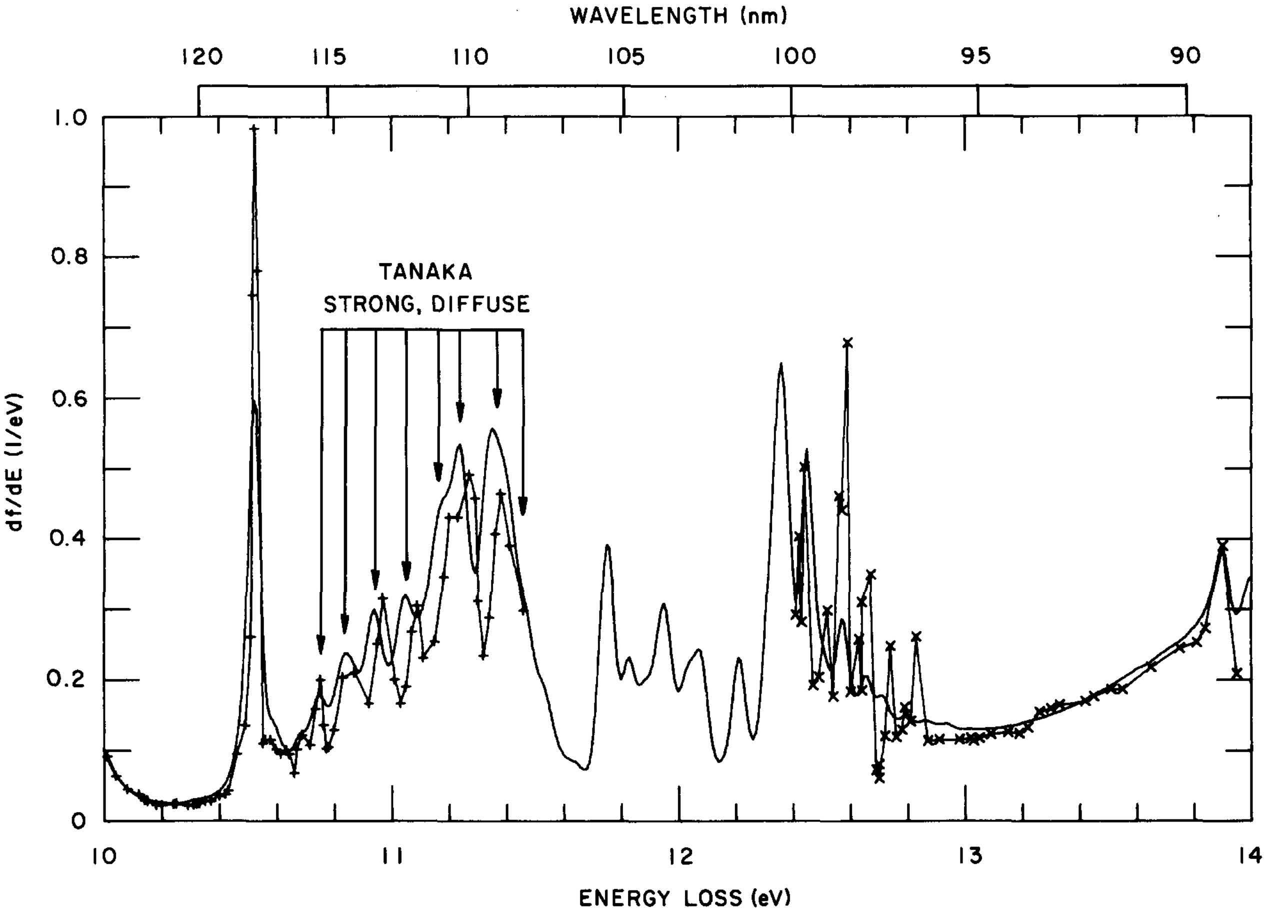

FIG. 3. Comparison of optical and electron-impact oscillator strengths in the 10–14 eV region: +, Ref. 16, ×, Ref. 13; solid line, present results.

an interaction is also suggested by the observed difference in term values for the $3s\sigma$ members of the $^2\Pi$ and $^2\Sigma$ series, as noted by Betts and McKoy.[20] This indicates considerable mixing between the $7\sigma 2\pi^4 ns\sigma$ and $7\sigma^2 2\pi^3 np\pi$ excited Rydberg configurations. Coincidently these configurations are very similar to the valence configurations $7\sigma 2\pi^4 8\sigma$ and $7\sigma^2 2\pi^3 3\pi$ chosen by Chutjian and Segal[14] to describe the $\tilde{C}^1\Sigma^+ \leftarrow \tilde{X}^1\Sigma^+$ transition at 9.66 eV and perhaps need be considered in the calculation of the oscillator strength for that band. From the data shown in Fig. 3, we have determined integrated values of the oscillator strength for small energy-loss intervals in the 10 to 14 eV region. These values, presented in Table II, were obtained by numerical integration of the data between the tabulated energy limits E_1 and E_2. Because our energy resolution is limited, these intervals unavoidably include contributions from unresolved transitions within the specified intervals, and no attempt was made to separate these. The first column, labeled E_m, gives the peak energy of the major feature within the interval with additional minor features or shoulders (sh) given in parentheses. The peak energies agree to within ± 0.010 eV with the spectral features tabulated by Tanaka *et al.*[21] The last column of Table II summarizes the identifications commonly ascribed to the principle feature in each interval. No other integrated values are available for comparison in this region, although the generally good agreement with differential values obtained from the optical data (Fig. 3) particularly in the 13.0–13.8 eV region indicate that the present results should be quite reliable.

SUMMARY AND CONCLUSIONS

The apparent oscillator-strength distribution obtained for N_2O is in good agreement with available optical data, although a weak non-optical transition is indicated below 6 eV. Our measurements also indicate a somewhat larger excitation probability in the 7.8 to 9.0 eV region than previously indicated by optical measurements. This discrepancy may be the result of band width dependence in the optical measurements. If this is the case, then the vibrational levels of the upper state may not be as strongly predissociated as previously thought.

Our analysis provides reliable oscillator-strength values not previously available in the 10 to 14 eV region. Examination of the irregular intensity variation in the $np\pi$ and $np\sigma$ Rydberg series converging to the $^2\Pi$-ion limit suggests considerable interchannel interaction with the $ns\sigma$ series ($^2\Sigma^+$ ion core.) Hopefully our results will provide a stimulus for additional theoretical analysis of the N_2O transitions in this region. A tabulation of differential oscillator-strength values at 10

TABLE II. Oscillator strength for transitions in N_2O from 10 to 14 eV.

E_m (eV)	E_1 (eV)	E_2 (eV)	f value	Identification
Continuum	10.23	10.36	4.56×10^{-3}	
10.52	10.36	10.56	4.21×10^{-2}	Ryd. $3p\pi$, $3p\sigma$ ($^2\Pi$ core)
10.59 sh	10.56	10.64	1.00×10^{-2}	Tanaka weak band 1
10.68 sh	10.64	10.71	8.40×10^{-3}	Tanaka weak band 2
10.75	10.71	10.78	1.17×10^{-2}	Tanaka strong band 3
10.84	10.78	10.89	2.34×10^{-2}	Tanaka strong band 3
10.94	10.89	10.99	2.56×10^{-2}	Tanaka strong band 3
11.05	10.99	11.09	2.85×10^{-2}	Tanaka strong band 3
11.24	11.09	11.29	8.48×10^{-2}	Ryd. $3d\pi$ ($^2\Pi$ core)
(11.19 sh)				Tanaka strong band 3
11.35	11.29	11.67	1.10×10^{-1}	Ryd. $4s\sigma$ ($^2\Pi$ core)
(others)				Ryd. $3d$? ($^2\Pi$ core)
11.75	11.67	11.80	31.0×10^{-2}	Ryd. $4p\pi$, $4p\sigma$ ($^2\Pi$ core)
11.83	11.80	11.86	1.28×10^{-2}	Ryd. $4d$? ($^2\Pi$ core)
11.95	11.86	12.00	3.30×10^{-2}	Ryd. $4d\pi$ ($^2\Pi$ core)
(11.89 sh)				
12.07	12.00	12.14	2.60×10^{-2}	Ryd. $5s\sigma$ ($^2\Pi$ core)
(12.04 sh)				
12.21	12.14	12.26	1.85×10^{-2}	Ryd. $5p\pi$, $5p\sigma$ ($^2\Pi$ core)
12.36	12.26	12.41	5.99×10^{-2}	Ryd. $3s\sigma$ ($^2\Sigma^+$ core)
12.45	12.41	12.53	4.20×10^{-2}	Ryd. $6p\pi$, $6p\sigma$ ($^2\Pi$ core)
12.57	12.53	12.62	2.10×10^{-2}	Ryd. $7p\pi$, $7p\sigma$ ($^2\Pi$ core)
12.65	12.62	12.69	1.33×10^{-2}	Ryd. $8p\pi$, $8p\sigma$ ($^2\Pi$ core)
12.71	12.69	12.76	1.14×10^{-2}	Ryd. $9p\pi$, $9p\sigma$ ($^2\Pi$ core)
12.79	12.76	12.83	1.01×10^{-2}	
12.86	12.83	12.90	9.77×10^{-3}	
continuum	12.90	13.80	1.57×10^{-1}	Portion of $^2\Pi$ ionization cont.
13.90	13.80	13.95	4.89×10^{-2}	Ryd. $3p\sigma$ ($^2\Sigma^+$ core)
14.00	13.95	14.09	4.39×10^{-2}	Ryd. $3p\pi$ ($^2\Sigma^+$ core)

intervals throughout the region investigated in this work is available upon request.

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