HIGH-RESOLUTION PHOTOABSORPTION AND PHOTOIONIZATION SPECTRA OF HD AND D_2

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Relative photoabsorption and photoionization cross sections for D_2 and HD are reported in the wavelength region between approximately 805 Å and 735 Å. Many members of the $np\sigma\ ^1\Sigma_u^+$ and $np\pi\ ^1\Pi_u$ Rydberg series for low n and low v were identified from previous assignments. An attempt was made to extend the assignments to higher vibrational quantum numbers for n = 3-6, using previously reported spectroscopic constants. This attempt was only moderately successful because of the overlap of vibrational bands at higher v. The increasing complexity of the spectra at high v and at high n requires a more sophisticated analysis such as would be provided by multichannel quantum defect theory (MQDT).

Ionization efficiencies were calculated for all identified states. The ionization efficiency was 1 for states which can autoionize by $\Delta v = 1$, i.e., the final state of the ion has a vibrational quantum number 1 less than the autoionizing state. In general, the ionization efficiency drops rapidly with $\Delta v > 1$. The $3p\pi\ ^1\Pi_u$ state, which can autoionize only with a $\Delta v \geq 7$, has essentially an ionization efficiency of zero, so decay must proceed by predissociation or molecular fluorescence.

Introduction

The photoabsorption spectrum from the ground rotational state of molecular HD or D_2 consists of two interacting Rydberg series converging to each vibrational level of the ion core. The lower members of the series correspond to $np\sigma\ ^1\Sigma_u^+$ and $np\pi\ ^1\Pi_u$ series of states, but as n increases there is a transition from Hund's case (b) to Hund's case (d) as a result of the effects of ℓ uncoupling, and the series converge, respectively, to the N = 0 and N = 2 rotational levels of the ion core. During the course of the ℓ uncoupling the two series perturb each other strongly, resulting in large energy level shifts and intensity variations. In addition to these interactions between the series converging to the same vibrational level of the ion ($\Delta v = 0$ interactions), there may be further

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intense perturbations from low n Rydberg states convering to higher excited vibrational states of the ion ($\Delta v \neq 0$ interactions).

The present work reports high resolution (0.016 Å, FWHM) relative absorption and photoionization cross sections for HD and D_2 at 78°K in the region from the ionization threshold to approximately 740 Å.

We were able to identify many peaks based on previous assignments made by Monfils[1,2] and by Takezawa and Tanaka[3,4] from very high resolution photoabsorption spectra. An attempt was made to extend these assignments by using (1) the vibrational and rotational term value expansion coefficients determined by the above workers and (2) the theoretical calculations of Kolos and Rychlewski[5] for the $3p\pi\ ^1\Pi_u$ state. We were aided by being able to observe the states in both absorption and ionization. For example, a state with low principal quantum number, which must autoionize with a large change in v, would be expected to have an ionization efficiency less than 1.

Experimental

A detailed description of the apparatus can be found in references 6 and 7. Only a brief summary will be given here.

The light source was the Hopfield helium continuum pulsed at 100 kc/sec. The light was monochromatized with a 3 m near-normal incidence monochromator before entering the ionization chamber. The ions were extracted from the chamber, focussed, and then passed through a quadrupole mass spectrometer for detection. Sample gas pressure was on the order of 10 μm. The resolution of the apparatus was observed to be 0.016 Å (FWHM) using 10 μm slits in 3rd order. Scanning was done in increments of 1/300 Å using a completely automated system.

Ordinary D_2 was used straight from commercial cylinders at 99.5% purity without further purification. Hydrogen deuteride was made by the hydrolysis of lithium aluminum hydride with deuterium oxide. The HD produced was about 94% pure with impurities of 5% H_2 and 1% D_2. The samples were cooled to liquid nitrogen temperature (78°K) before entering the ionization chamber.

Slippage in the wavelength drive resulted in shifts in the absolute wavelength scale of about 0.03 Å in both the positive and negative direction throughout the scanning range. Consequently, accurate absolute wavelengths are best taken from plate spectra, such as those taken by Monfils[1,2] and Takezawa and Tanaka.[3,4]

Results and Discussion

Spectra

Figures 1 and 2 show transmitted light and ionization plotted on the same wavelength scale for D_2 and HD, respectively, starting near their ionization thresholds. The data for D_2 were obtained from one continuous run. For HD, the data were collected from three separate runs. Each run was scaled, using the overlap between them, so that the final plot represents a smooth continuous spectrum.

Assignments

Our spectra were simplified because the samples were cooled to liquid nitrogen temperature, so only transitions originating in the lower rotational levels were observed. We began by using previously published assignments. First, considering D_2, we were able to identify transitions to the $3p\pi$ state for $v = 9\text{-}15$, using assignments made by Monfils.[1] Then, with the assignments of Takezawa and Tanaka,[4] all the $np\sigma$ and $np\pi$ transitions ($n = 4\text{-}6$) that they identified in our wavelength region were identified. Also, some higher lying states ($n \leq 10$) were identified from assignments by Takezawa and Tanaka.[4] For HD the $3p\pi$, $v = 7,8$ and $4p\pi$, $v = 5,6$ can be found, based on the assignments of Monfils.[1] In some cases peaks were reassigned on the basis of relative intensities in absorption and ionization.

We next extended our assignments using publishes constants. Extension of $3p\pi$ transitions was the easiest to make using our data since they distinguish themselves by negligibly autoionizing. From the expansion coefficients for the $3p\pi$ state given by Monfils[1,2] and the theoretical energy levels calculated by Kolos and Rychlewski,[5] we were able to assign the $3p\pi$ state transitions very nearly to the dissociation limit. Several other new assignments are also shown in Figures 1 and 2.

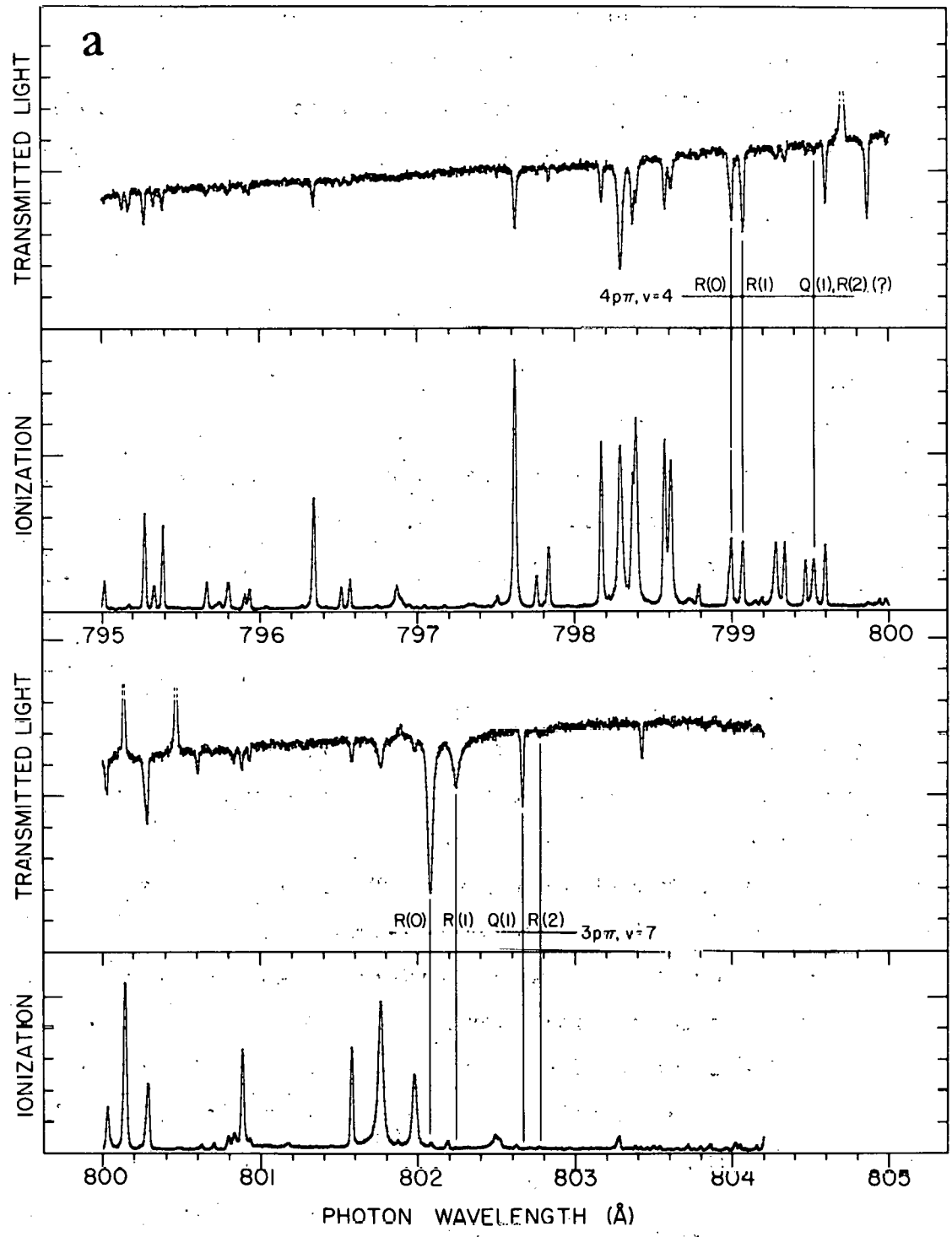


FIG. 1.--Relative photoabsorption and photoionization cross sections for HD taken at a wavelength resolution of 0.016 Å and a temperature of 78°K.

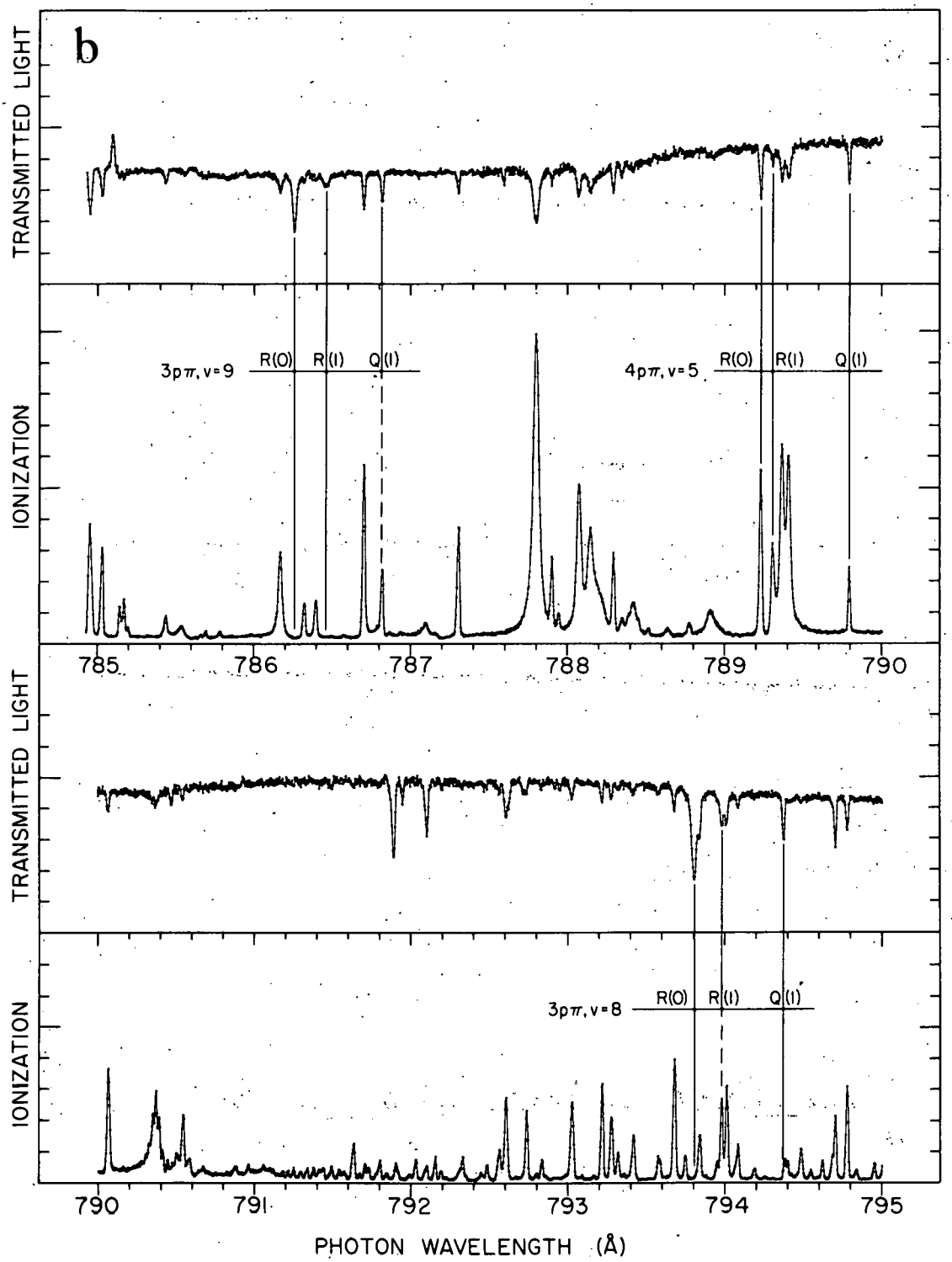
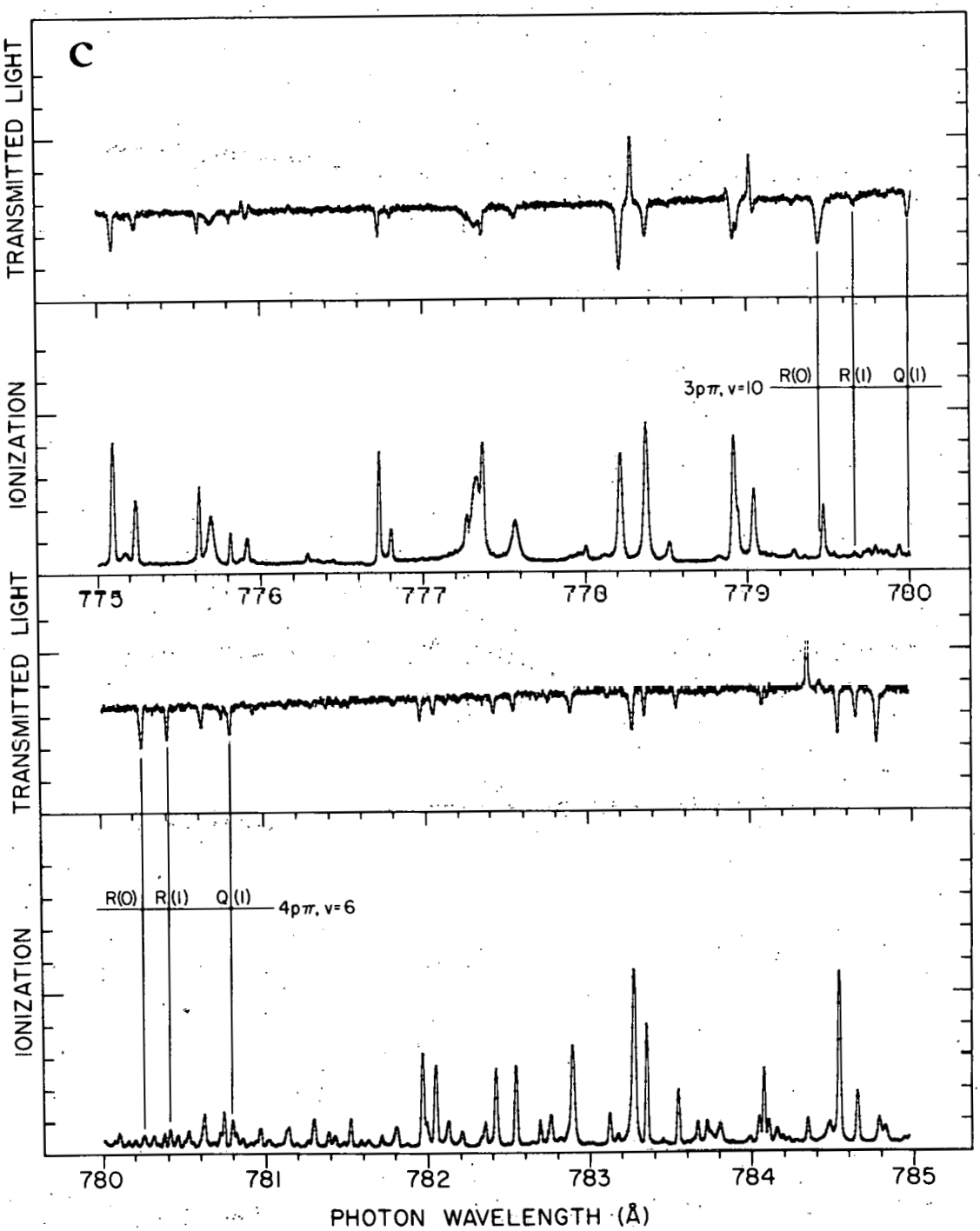


FIG. 1.--continued.



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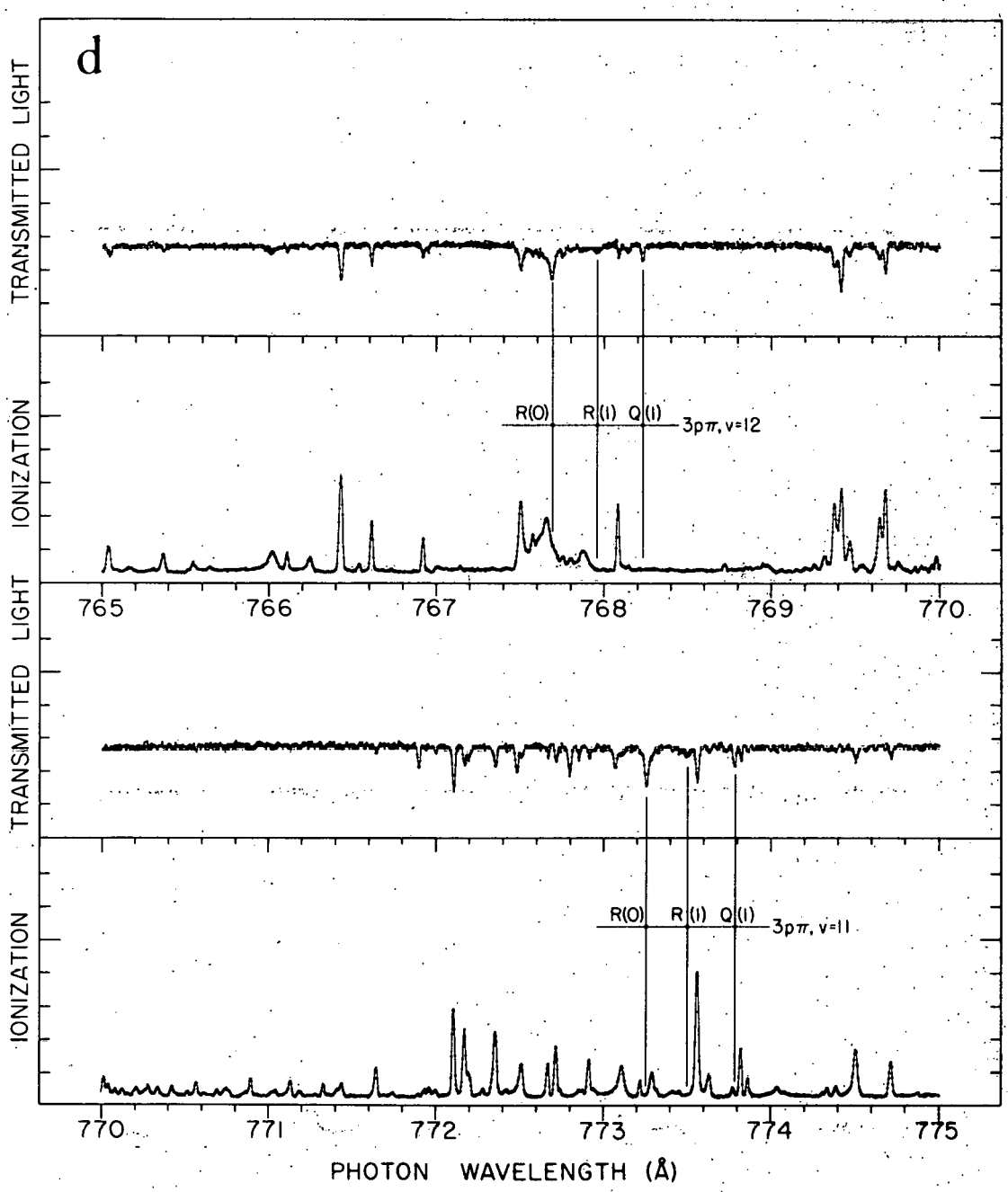

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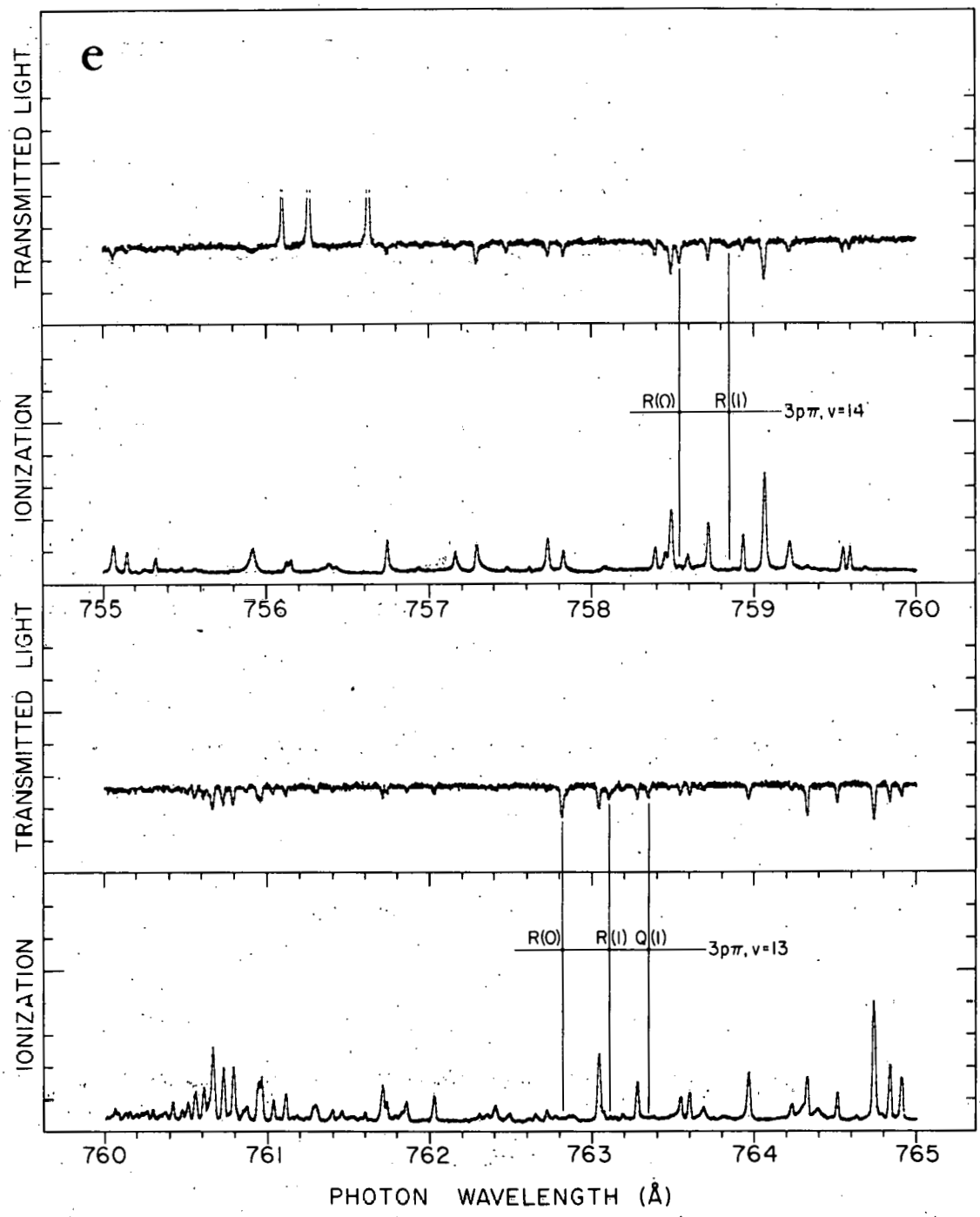

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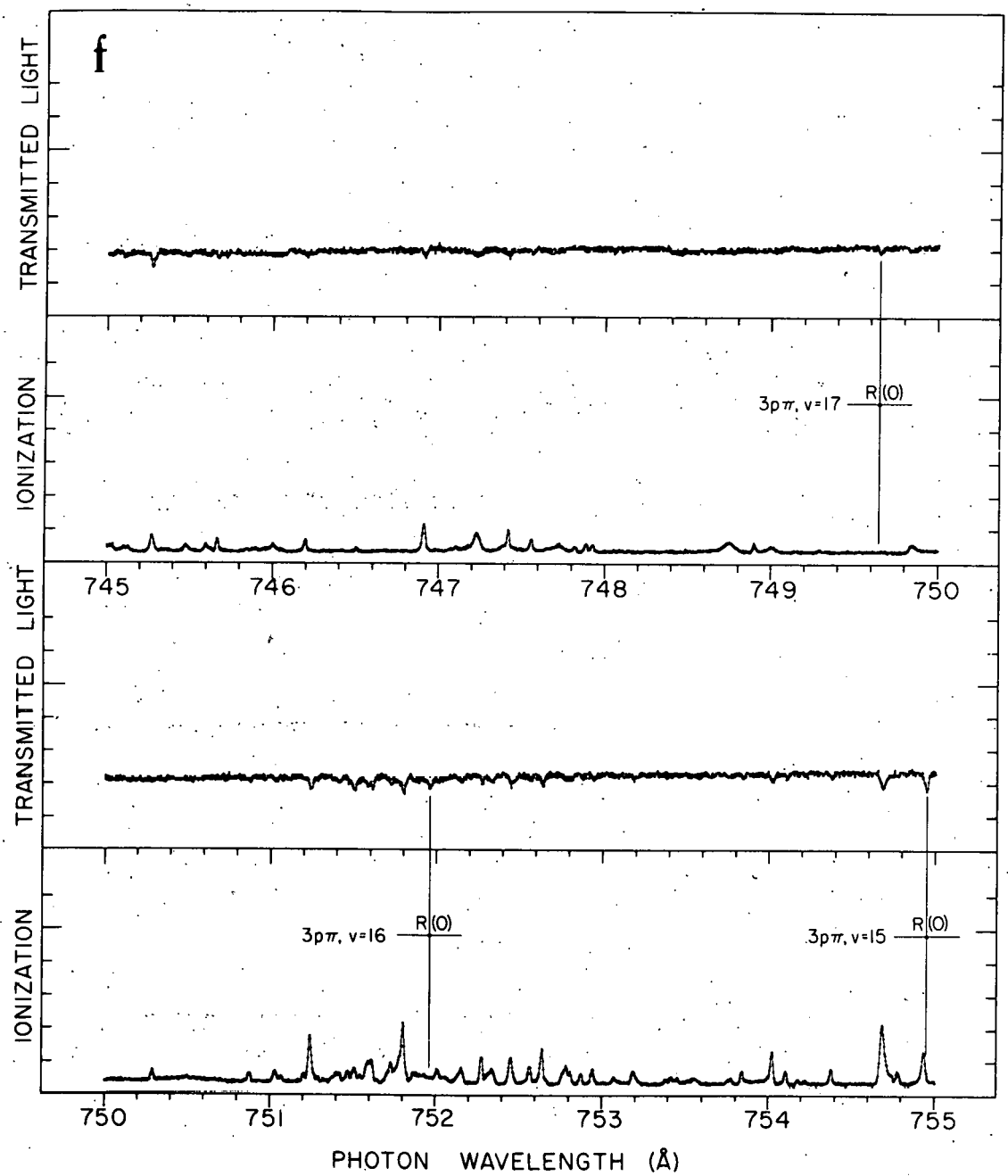

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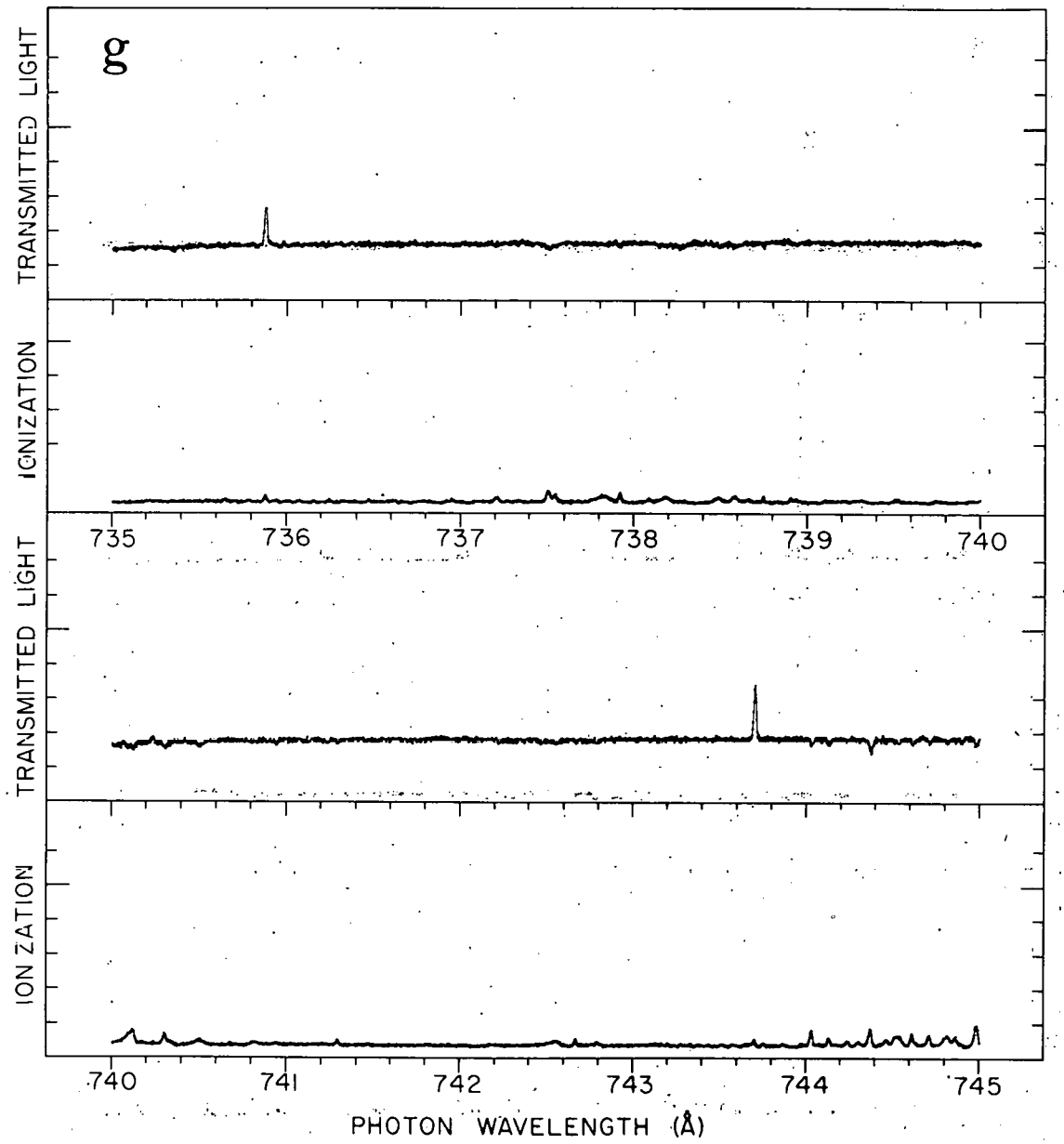


FIG. 1. continued.

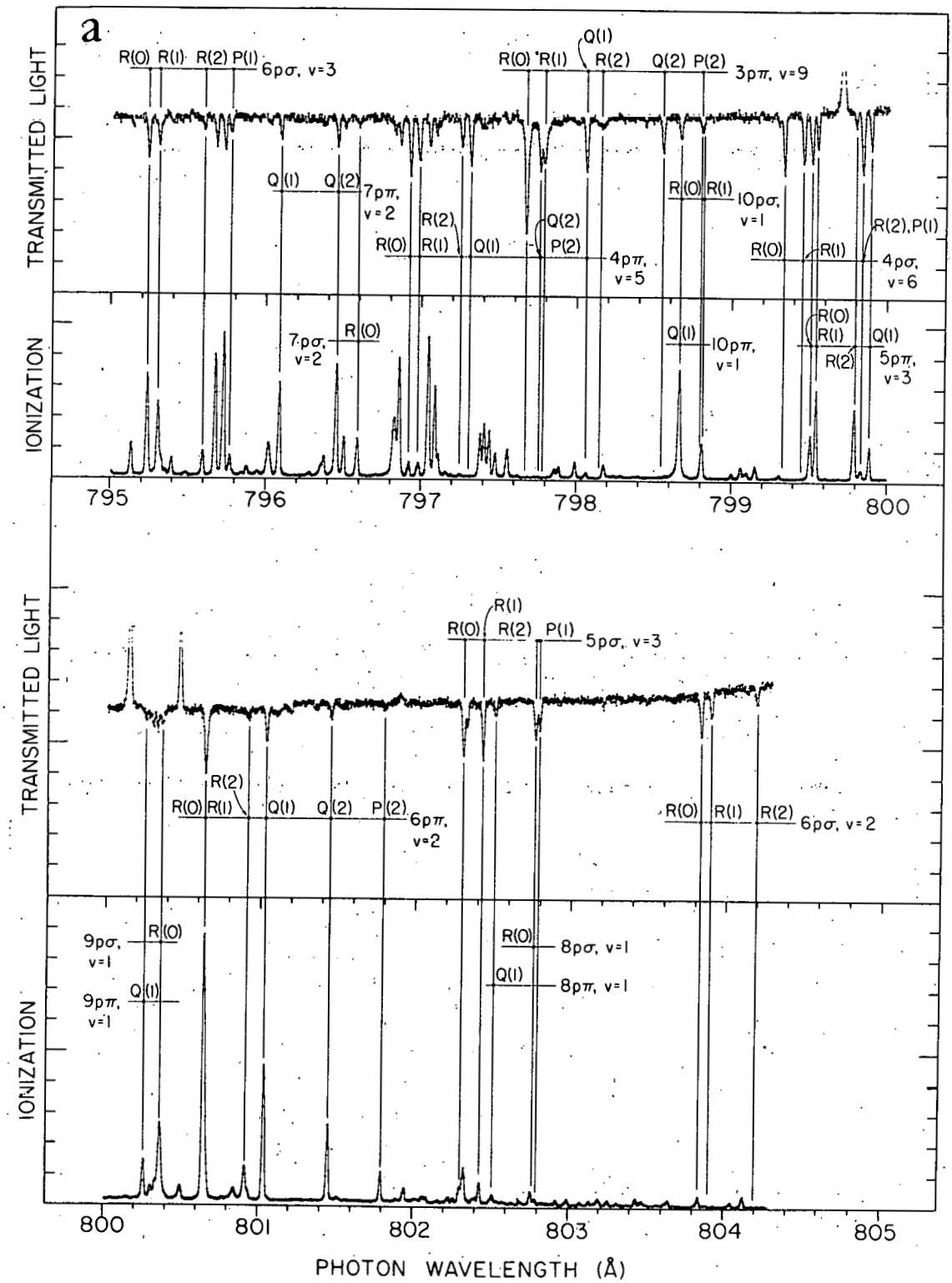
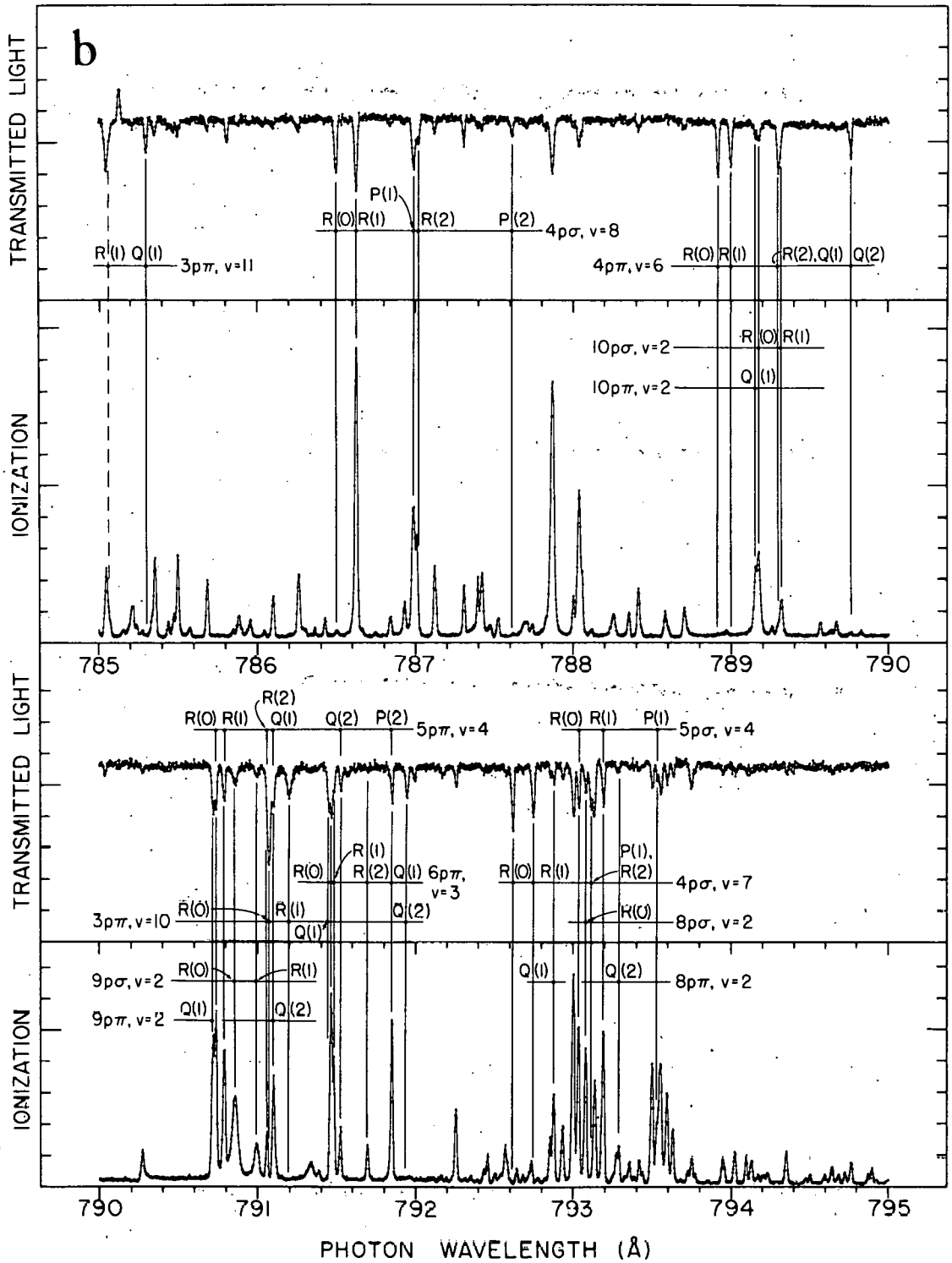


FIG. 2.--Relative photoabsorption and photoionization cross sections for D_2 taken at a wavelength resolution of 0.016 Å and a temperature of 78°K.



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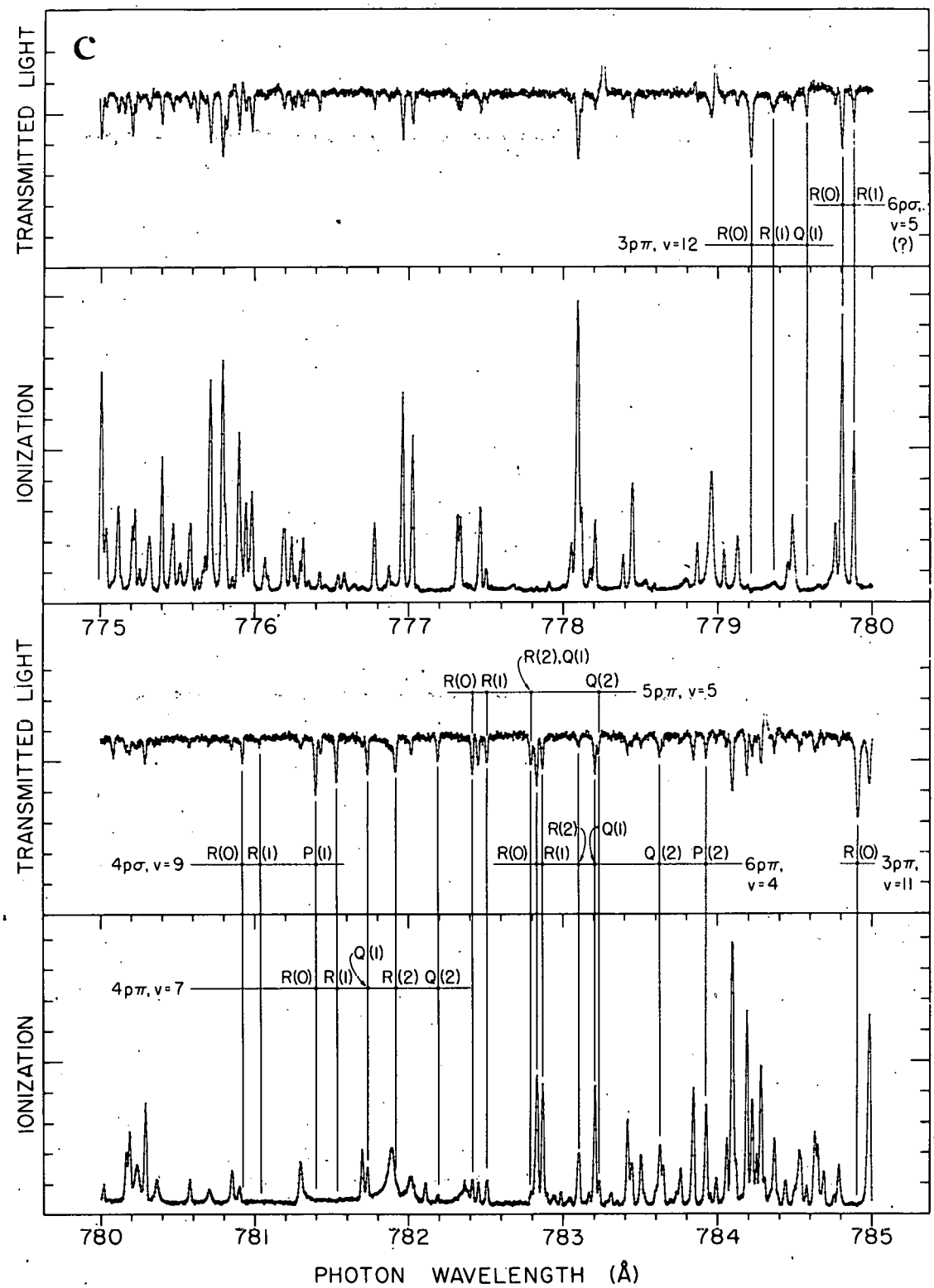

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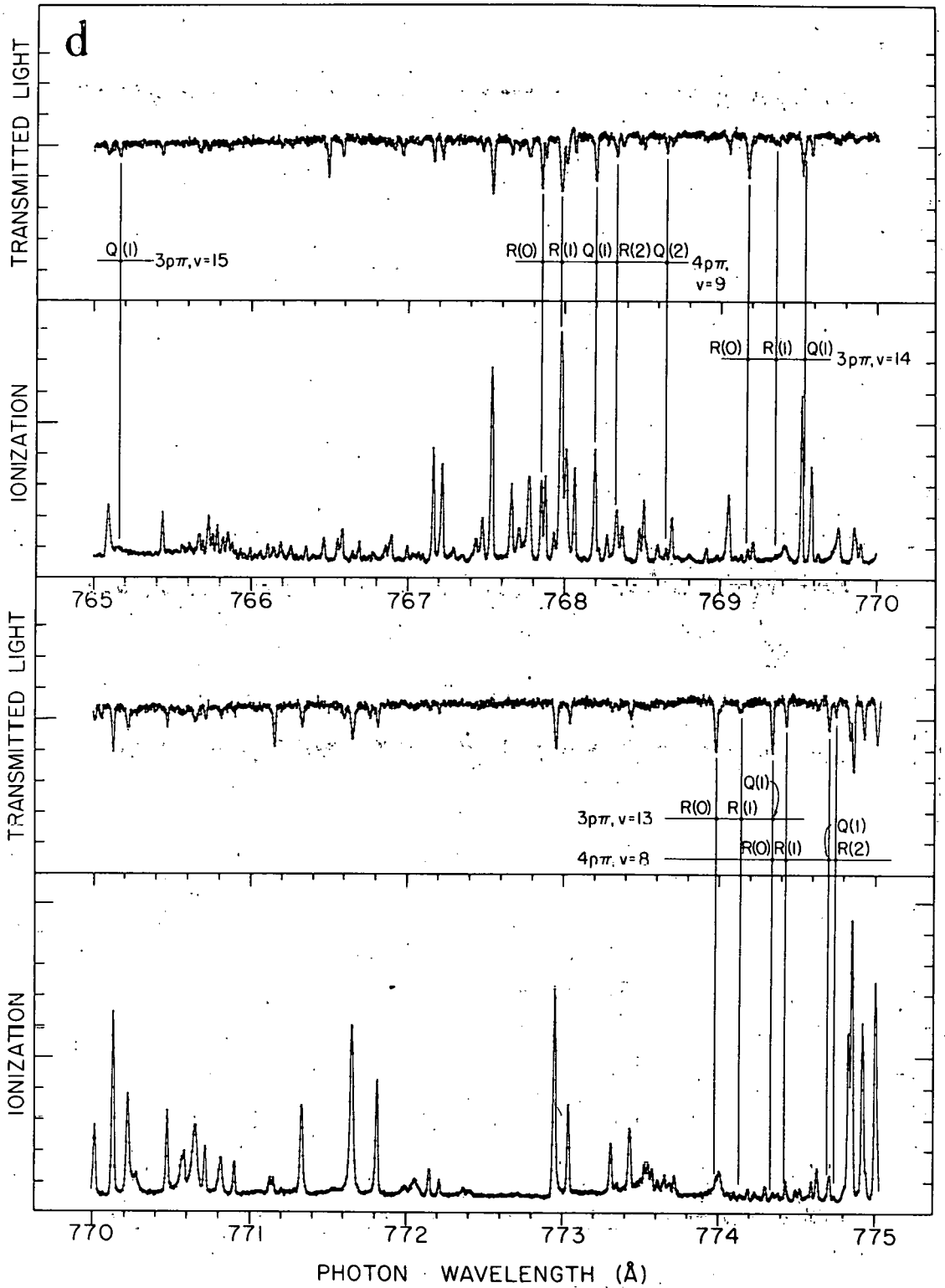

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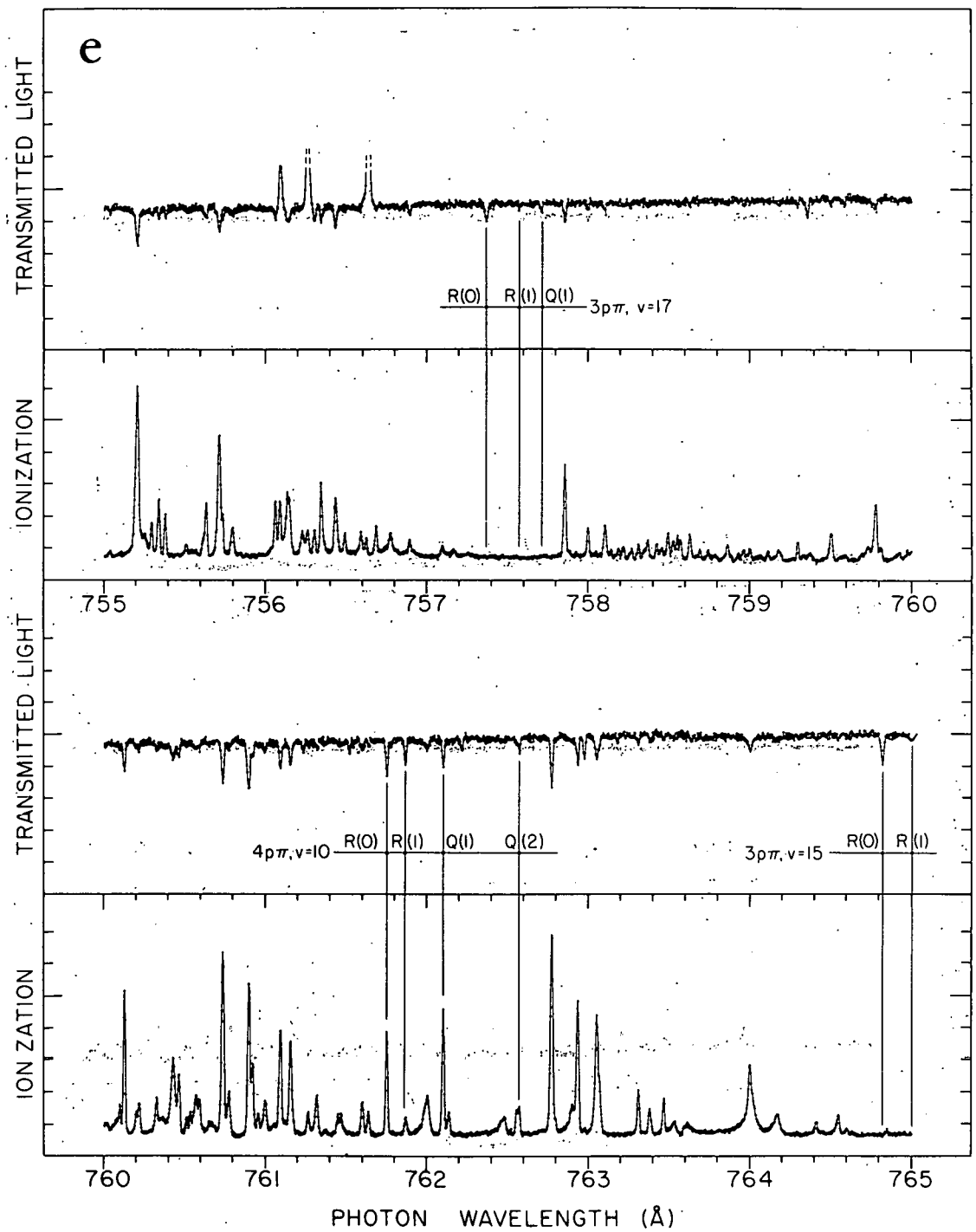

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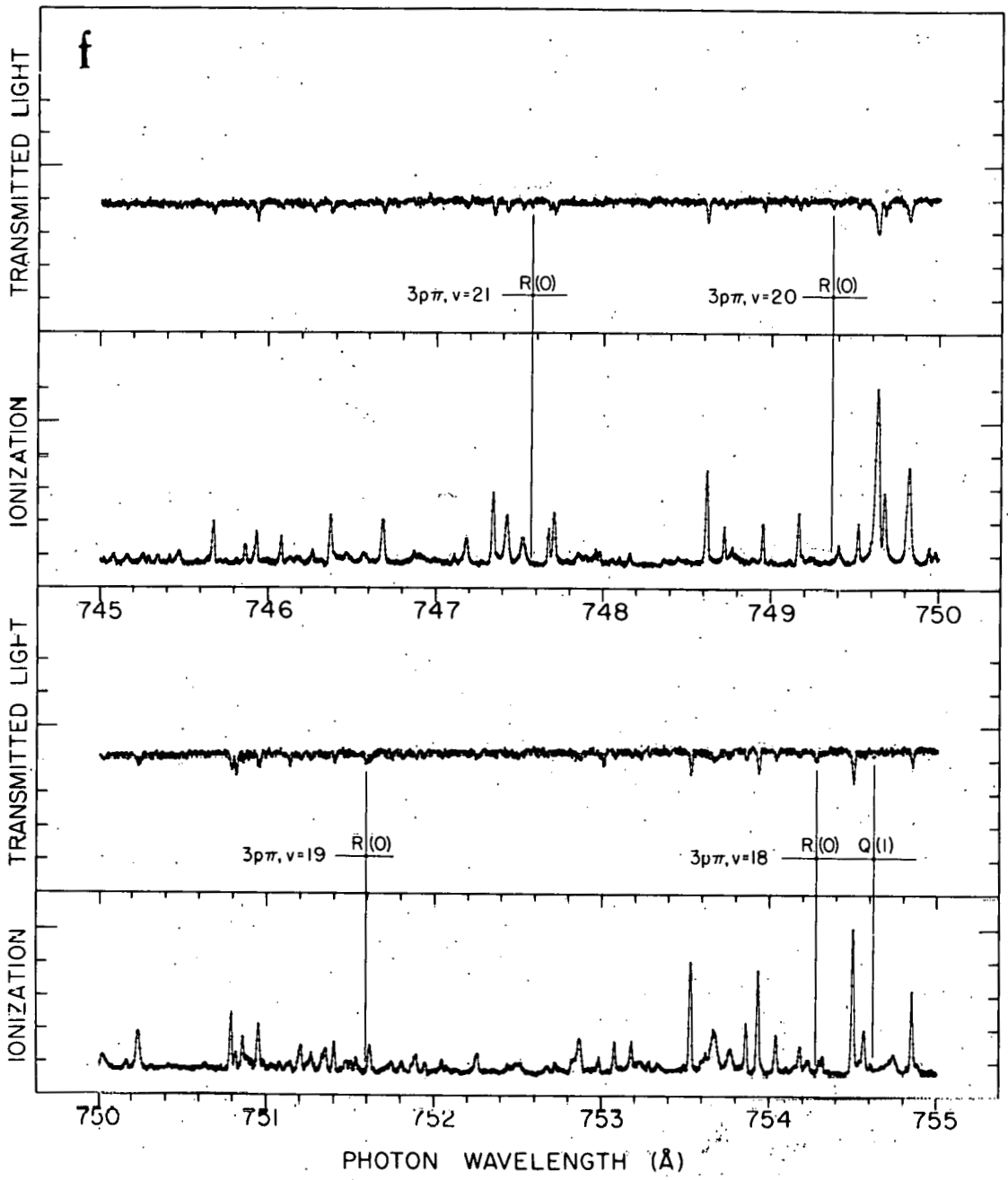

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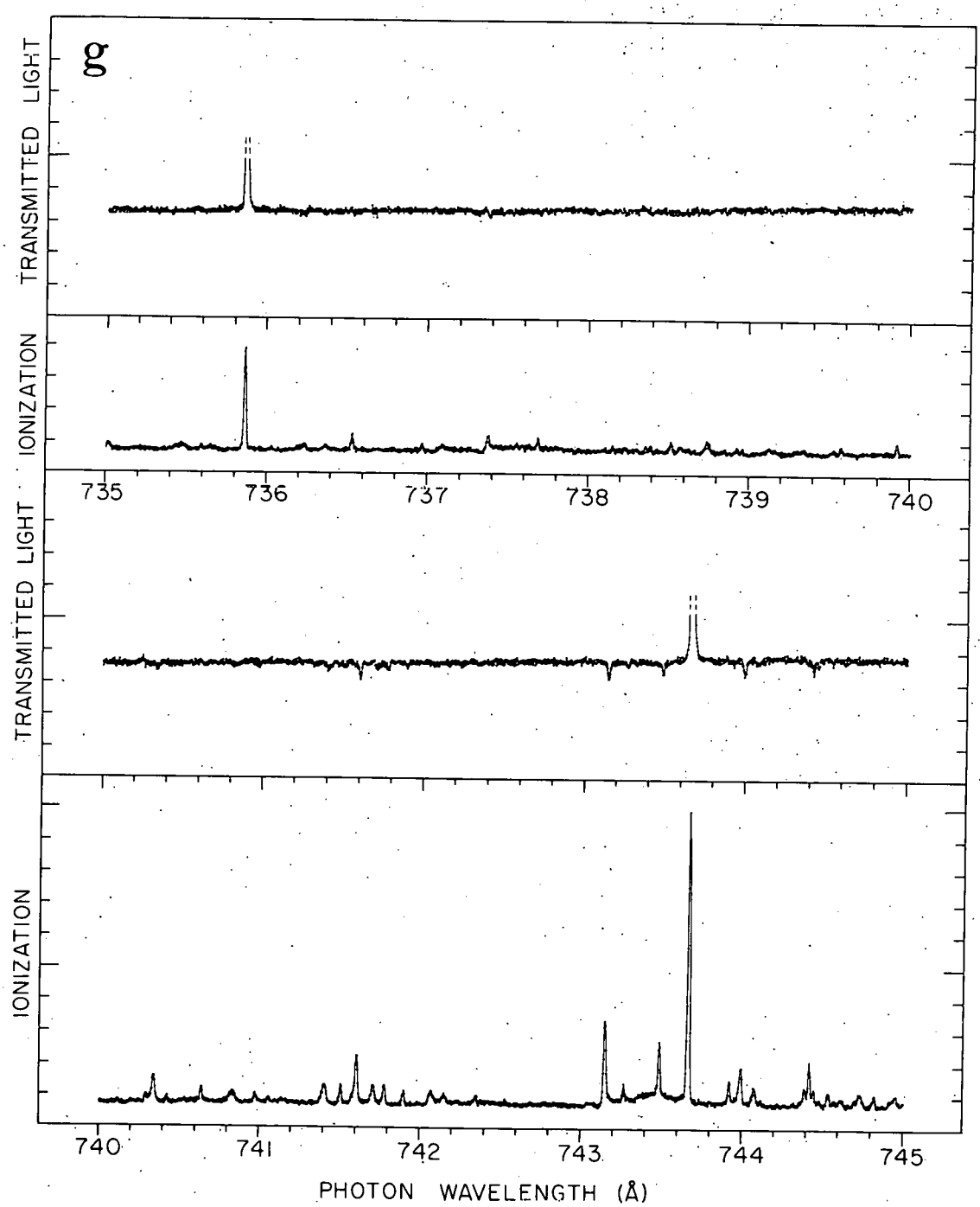

FIG. 2.--continued.

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