

Erratum: Infrared Absorption by Peroxy-Nitrogen Trioxide Free Radical in the Gas Phase

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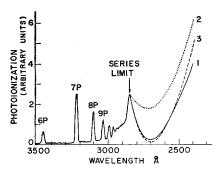


Fig. 1. Photoionization spectrum of potassium vapor at 149°C. (1) Present results, (2) Ditchburn et al., (3) Bates (theoret.). All the curves have been normalized to the same value at the series limit, although in fact Bates and Ditchburn et al. differ by almost a factor of 2.

ion detector. This chamber was located in an oven and was connected to a vacuum system capable of 10⁻⁶ torr.

The potassium vapor was irradiated through the sapphire window with light from a Bausch & Lomb high-intensity grating monochromator with xenon light source and the rate of production of ions measured as a function of wavelength. The light from the monochromator was modulated by a disc chopper and the ion detector signal measured using a synchronous amplifier. The ion detector signal was recorded as a function of wavelength and divided by the spectrum of the source-monochromator combination, as specified by Bausch & Lomb, to obtain the photoionization spectrum. The Kingdon Cage ion detector is not a suitable instrument for measuring absolute photoionization currents so the ordinate is given in arbitrary units.

In the continuum region, at wavelengths shorter than the series limit, theoretical and experimental absorption and photoionization spectra are shown for comparison. It is seen that the present results agree better with the theory of Bates⁵ than do the photoabsorption measurements of Ditchburn. The difference between the present results and the earlier photoionization results2,3 is explainable by the improved resolution in the present case. The series of peaks which merge to form a false continuum on the long-wavelength side of the series limit correspond to the principal series lines of potassium. A detailed study of the phenomenon of photoionization by line absorption in cesium was made by Mohler and Boeckner.6 In the present case, the wavelength threshold for this effect in potassium was found

to lie between the 5P and 6P peaks, as was also observed by Lee and Mahan. Interpreting this according to the conclusions of Mohler and Boeckner, 6 as was done for the other alkali metals by Hudson,7 yields a value of 3.58 eV < (I.P.)m < 4.11 eV for the ionization potential of the K_2 molecule and 0.74 eV $< D_0^+ < 1.27$ eV for the K_2^+ ion. The value of D_0^+ is in agreement with the 0.76 eV calculated by Robertson and Barrow⁸ from molecular spectra.

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Further investigation with a substantially improved experimental system (single-beam analysis instead of double beam, steady-state flow instead of batch runs, substantial reduction of water vapor, greatly improved resolution) has shown that the reported change of intensity of infrared absorption on the shoulder of the Pbranch of nitric oxide at 1840 cm⁻¹ was not due to OONO. It appears that reproducible systematic error led to an erroneous correction for N2O3, and the reported band was additional N2O3, not OONO. If any species other than NO, N2O3, NO2, or N2O4 absorbs in the region 1800-1900 cm⁻¹, its optical density is less than 2% of that erroneously ascribed to OONO.