NGR-28-004-021

(NASA-CR-139676) VIBRATIONAL INTENSITY DISTRIBUTIONS FOR CONTINUUM PHOTOIONIZATION OF OXYGEN (Nebraska Univ.) 5 p HC $4.00 CSCL 07D
N74-31602
Unclas
G3/06 48148

Vibrational Intensity Distributions for Continuum Photoionization of Oxygen

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We have recently reported experimental vibrational intensity distributions for continuum photoionization of N_2 and CO, mainly at a wavelength of 584 Å.[1] the purpose of this note is to report similar results for oxygen using both the 584 Å and 304 Å helium lines.

The photoionization cross section of oxygen shows a substantial dip in magnitude over a 20 Å band centered about 590 Å;[2] thus the possibility exists that the 584 Å photoelectron spectrum of oxygen includes an autoionized contribution and, consequently, the vibrational intensity distributions may not correspond to those of continuum ionization. The oxygen photoionization cross section shows no structure around 304 Å and purely continuum ionization is expected.

The experimental technique is that reported previously.[1] Photoelectron spectra were recorded at a resolution of 45 meV with dispersed He radiation, using a cylindrical mirror energy analyzer with known transmission properties.

The vibrational intensity distributions at each wavelength were corrected for the transmission of the analyzer and normalized to 100 at the strongest level. The results are presented in table 1 together with calculated Franck-Condon factors.[3] The error bars for the 584 Å data represent standard deviations from averaging a number of results; the error bars for the 304 Å data were generated from the statistics of the single 304 Å spectrum.

All of the distributions are in reasonable agreement with those of Edqvist et al.[4] For transitions to O_2^+ $X\ ^2\Pi_g$, the 304 Å distribution agrees more closely with the Franck-Condon factors. The error bars for the two distributions do not overlap, indicating that some of the 584 Å distribution may come from autoionization. The 584 Å and 304 Å experimental distributions and the Franck-Condon factors for transitions to the $a\ ^4\Pi_u$ state of O_2^+ are in close agreement, indicating that the transitions represent purely continuum ionization (data are only compared up to the v=7 level since higher levels of the $a\ ^4\Pi_u$ state were not resolved from the $A\ ^2\Pi_u$ state).

The intensity distributions for transitions to the $b\ ^4\Sigma_g^-$ state of O_2^+ are markedly different, with the 304 Å data showing the best agreement with the Franck-Condon factors. We have been measuring photoelectron branching ratios for oxygen at a series of photon wavelengths and then computing partial photoionization cross sections. These results, to be published elsewhere, show that most or all of the dip in the cross section near 590 Å appears in the cross section for production of the b $^4\Sigma_g^-$ state. Thus, this state could be expected to show a perturbed vibrational distribution at 584 Å.

No Franck-Condon factors have been calculated for transitions to the B $^2\Sigma_g^-$ state of O_2^+; this state predissociates and has not been detected in emission.[3] With the exception of the v=4 level, the distributions for the two exciting wavelengths are in reasonable agreement.

The distributions shown in table 1 for 304 Å radiation should correspond to continuum ionization. Evidence supporting this statement is the close agreement (within a few percent) between the vibrational intensity distributions in the 304 Å photoelectron spectra of N_2 and CO[5] and the previously reported distributions[1] at longer wavelengths. The only disagreement occurs in the distribution over the N_2^+ ground state; transitions to this level have also been shown to have anomalous angular distributions.[6]

Acknowledgement.

This research was supported in part by the National Aeronautics and Space Administration and the Atmospheric Sciences Section of the National Science Foundation.

References

1. J. L. Gardner and J. A. R. Samson, J. Chem. Phys. 60, 3711 (1974).

2. L. C. Lee, R. W. Carlson, D. L. Judge and M. Ogawa, J. Quant. Spectrosc. Radiat. Transfer 13, 1023 (1973).

3. P. H. Krupenie, J. Phys. Chem. Ref. Data 1, 423 (1972).

4. O. Edqvist, E. Lindholm, L. E. Selin and L. Åsbrink, Phys. Scripta 1, 25 (1970).

5. J. L. Gardner and J. A. R. Samson, unpublished data.

6. T. A. Carlson, Chem. Phys. Lett. 9, 23 (1971).

TABLE 1. Vibrational intensities and Franck-Condon factors for transitions O_2 X $^3\Sigma_g^-$ (v=0) to the O_2^+ levels indicated

		Experimental Intensity		
		584 Å	304 Å	FCF[3]
X $^2\Pi_g$	v=0	46.4 ± 2.3	54.9 ± 2.6	51.7
	1	100.0 ± 3.0	100.0 ± 3.1	100.0
	2	94.0 ± 1.3	81.3 ± 2.9	79.6
	3	45.2 ± 2.3	31.5 ± 2.2	33.7
	4	13.8 ± 1.7	7.6 ± 2.0	8.17
	5	1.4 ± 0.2		1.14
a $^4\Pi_u$	v=0	9.4 ± 1.2	11.5 ± 4.7	7.58
	1	29.2 ± 2.8	24.3 ± 4.5	27.8
	2	55.6 ± 3.9	66.1 ± 6.0	55.7
	3	80.2 ± 5.3	75.2 ± 6.3	81.3
	4	92.0 ± 5.3	92.3 ± 6.4	96.8
	5	100.0 ± 2.9	100.0 ± 6.5	100.0
	6	92.5 ± 5.5	80.6 ± 6.0	93.1
	7	88.2 ± 3.8	73.2 ± 5.7	
b $^4\Sigma_g^-$	v=0	100.0 ± 3.2	100.0 ± 3.7	100.0
	1	86.8 ± 2.2	70.6 ± 3.3	82.4
	2	54.3 ± 0.6	34.0 ± 2.8	40.1
	3	33.7 ± 1.0	12.7 ± 2.4	15.3
	4	18.4 ± 2.6	3.9 ± 2.1	
	5	5.2 ± 0.5		
B $^2\Sigma_g^-$	v=0	86.2 ± 8.5	86.3 ± 6.1	
	1	100.0 ± 5.7	100.0 ± 6.3	
	2	80.2 ± 5.7	71.8 ± 5.8	
	3	51.9 ± 7.8	43.9 ± 5.3	
	4	35.3 ± 1.8	14.8 ± 4.7	
	5	12.2 ± 0.7	9.3 ± 4.6	
	6	1.4 ± 0.8		