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Photoelectron spectra of some polyatomic molecules

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The photoelectron spectra of ethylene, ethylene-d_4, ammonia, and ammonia-d_3 have been measured using a hemispherical high resolution electrostatic spectrometer and the 584 Å helium resonance line as the exciting radiation. Many ionization potentials have been determined for each compound and vibration structure associated with the transitions leading to the various ionization potentials has in many cases been well resolved. It has been possible to suggest reasonable assignments for the corresponding vibrational modes. The photoelectron spectra of $O_2^+ (^2\Pi_g)$ obtained using neon radiation (736 and 744 Å) shows a progression of twenty-one vibrational transitions, with maxima at $v = 1$ and $v = 7$. This is larger than the number of vibrational transitions observed with the 584 Å helium line and it is postulated that the extra structure observed arises from ionization processes from a long-lived excited state of oxygen.

INTRODUCTION

When a molecule is ionized after the absorption of a quantum of radiation $h\nu$, the resulting photoelectron has kinetic energy E. These quantities are related to the ionization potentials of the molecule by the Einstein equation (1)

$$E = h\nu - I_i - E_{\text{vib}} - E_{\text{rot}}, \tag{1}$$

where I_i represents one of the ionization potentials of the molecule. Energy analysis of the photoelectrons (Vilesov, Kurbotov & Terenin 1961; Al-Joboury & Turner 1963; Schoen 1964; Frost, McDowell & Vroom 1965) yields a photoelectron spectrum. If the energy analyser has high enough resolution fine structure may be revealed which is due to the excitation of vibrational motion in the molecular ion. Franck–Condon factors for molecular vibronic transitions can readily be estimated for comparison with computed values (Turner & May 1966; Frost, McDowell & Vroom 1967*a*). Since photoelectron spectra readily yield values for the various ionization potentials of molecules these and other important features of the spectra can be correlated with the results obtained from various molecular orbital theories of the electronic structures of molecules. Thus this type of investigation promises to be a fruitful new field in the study of molecular structure (Frost, McDowell & Vroom 1967*b*; Baker & Turner 1968; Dewar & Worley 1969).

Many types of energy analysis have been used in photoelectron spectroscopy. We recently constructed a hemispherical electrostatic analyser and have used it to obtain the high resolution photoelectron spectra recorded in this paper.

EXPERIMENTAL DETAILS

Figure 1 shows a schematic diagram of the hemispherical spectrometer. Photoelectrons leave the 10 mm diameter by 25 mm long collision chamber and enter the analyser through a cylindrical focusing lens system. The hemispheres are 42 and 58 mm in diameter, machined

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from brass and gold plated. The inner surface of the collision chamber is coated with benzene soot to minimize secondary electron scattering.

The detection system comprises a Mullard B 138 AL channel type multiplier, a Nuclear Enterprises pulse counting system (NE 5281 pre-amplifier, 4602 analyser, 4603 pulse amplifier and a 4607 ratemeter) and a Fabritek 1024 channel signal averager. The output is displayed on a Moseley XY plotter.

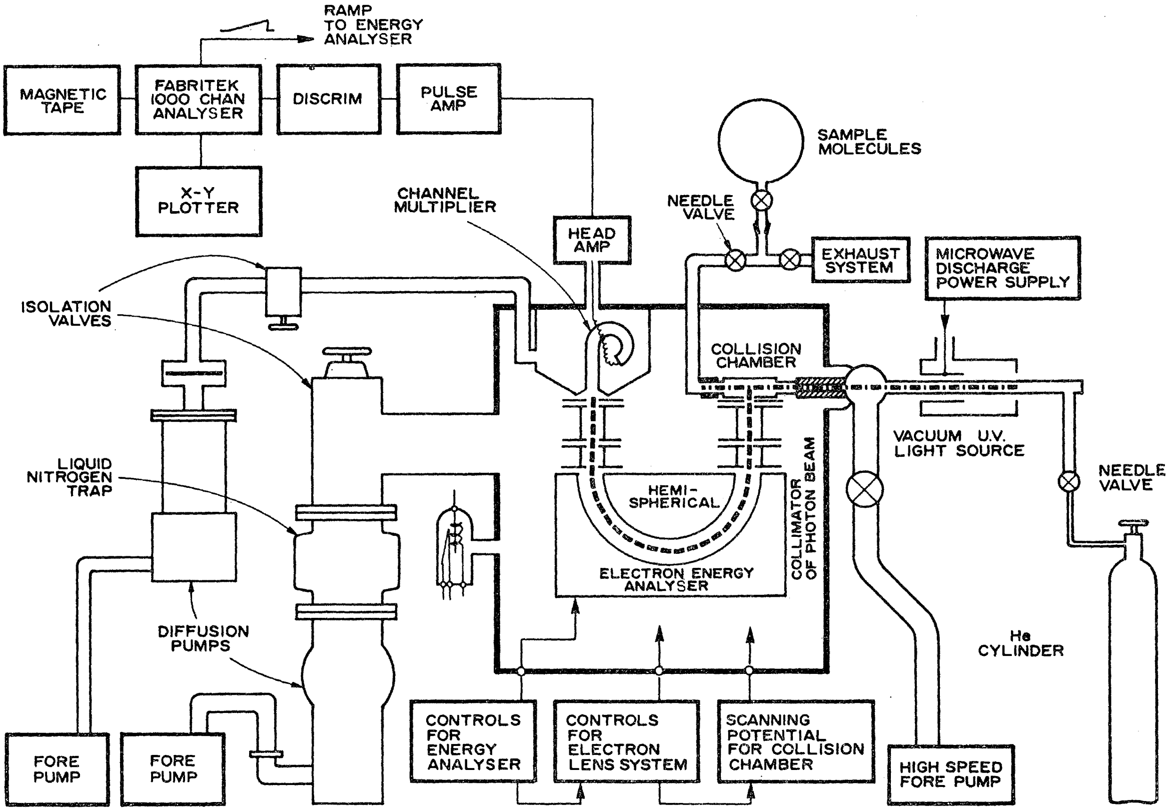

Figure 1. Schematic diagram of the hemispherical photoelectron spectrometer.

The sample is introduced into the collision chamber through a Granville Phillips variable leak, and the main chamber pressure is usually about 1.3 mN m^{-2} (10^{-5} Torr) during a run. The spectrum is scanned by varying the potential applied between the collision chamber and the centre tap of a resistor across the analyser hemispheres, which are normally set to focus 2 eV electrons. This mode of scanning ensures a constant resolution. The scanning potential is obtained by amplifying a 4 V ramp voltage originating from the multichannel analyser, the ramp also serving as an internal trigger for the multiple scan. A typical count rate for argon at a main chamber pressure of 1.3 mN m^{-2} (10^{-5} Torr) is 3000 s^{-1}.

The ethylene and ammonia were obtained from the Matheson Co., the ethylene-d$_4$ and ammonia-d$_3$ from Merck, Sharp and Dohme, and the oxygen from a commercial tank. Mass spectral analysis revealed no impurities capable of interfering with the photoelectron spectra.

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Results and discussion

Ethylene and ethylene-d$_4$

The photoelectron spectra of ethylene and ethylene-d$_4$ are shown in figures 2 and 3 respectively. There are clearly five ionization potentials associated with each spectrum. The xenon calibration peaks may also be seen.

The adiabatic values for the ionization potentials are listed in table 1, together with previous values found by Baker, Baker, Brundle & Turner (1968) and theoretical values based on an s.c.f. calculation by Robin, Hart & Kuebler (1966).

Ethylene is isoelectronic with oxygen, and its electron configuration (omitting carbon 1s^2) can be written, in order of increasing binding energy,

$$(2a_g)^2(b_{1u})^2(1b_{2u})^2(3a_g)^2(1b_{3g})^2(1b_{3u})^2,\ {}^1A_g$$

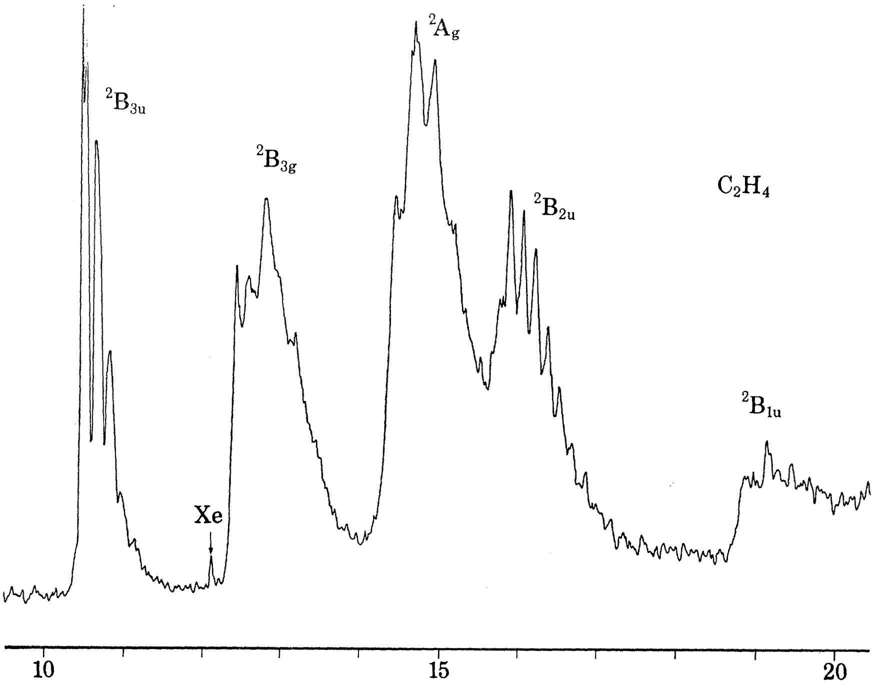

Figure 2. Photoelectron spectrum from ethylene obtained using the 584 Å helium resonance line.

The first ionization potential was calculated by Mulliken (1949) to be 10.56 eV, in good agreement with the experimental value of 10.51 eV and the theoretical value of 10.57 eV obtained by Robin *et al.* (1966). The degree of hybridization of some of the higher orbitals cannot be accurately assessed, and so Mulliken did not estimate the corresponding ionization potentials. However, the $(2a_g)^2$ is strongly C—C bonding, whereas the $(2b_{1u})^2$ is antibonding (although it might be bonding with respect to CH_2 as well).

The first ionization potential refers to the removal of a π electron, and the associated band in the photoelectron spectra shows a progression in ν_2. The resulting ion is probably non-planar with a torsional angle of 25°. ν_3 is assigned on the basis of a shoulder on and broadening of the second peak of the first band of both C_2H_4 and C_2D_4. Thus the observed spectrum is very similar to the electronic spectrum for the first Rydberg ($\tilde{B}$) state of ethylene, which shows a

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vibrational progression assignable to $2\nu_4$ superimposed on that due to ν_2. The suggested assignments are given in table 2.

Both second and third ionization potentials refer predominately to the CH bonding orbitals ($1b_{3g}$) and ($3a_g$). Calculations have predicted the former to be the higher orbital (Kaldor &

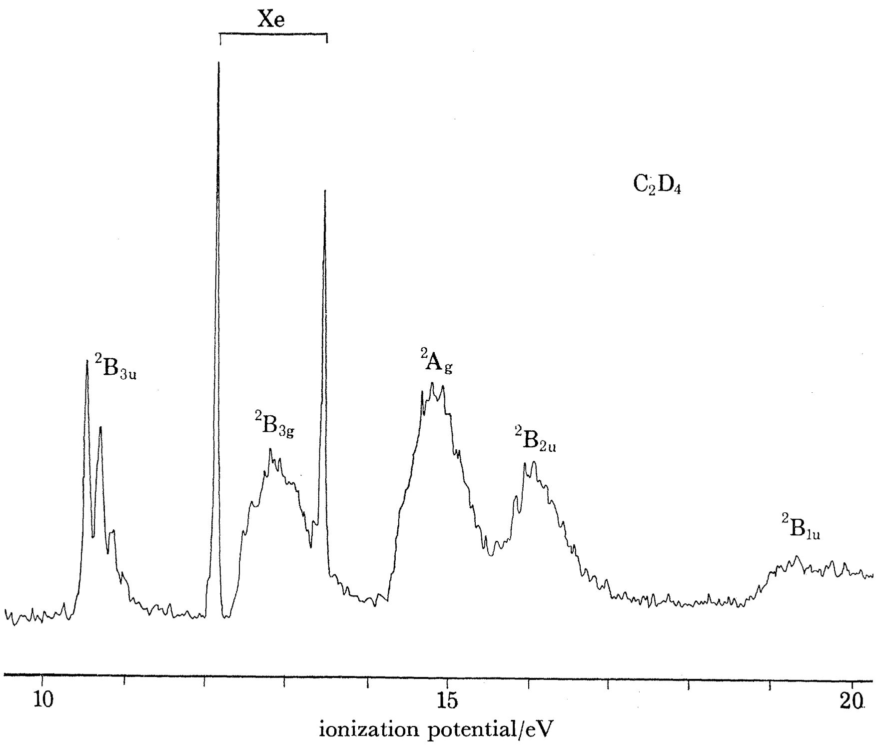

FIGURE 3. Photoelectron spectrum from ethylene-d_4 obtained using the 584 Å helium resonance line.

TABLE 1. IONIZATION POTENTIALS OF C_2D_4 AND C_2D_4 (eV)

	theoretical.	photoelectron spectroscopy		
	Robin *et al.* (1966)	Baker *et al.* (1968)	present work	
ionic state	C_2H_4	C_2H_4	C_2H_4	C_2D_4
$^2B_{3u}$†	10.57	10.51	10.51	10.52
$^2B_{3g}$	10.31	12.38	12.46	12.48
^2A_g	15.40	14.47	14.46	14.45
$^2B_{2u}$	17.54	15.68	15.78	15.83
$^2B_{1u}$	21.40	18.87	18.87	18.90

† This is based on the ion having D_{2h} symmetry. If, as is more probable, the symmetry is D_2, the state should be classified as $^2B_3$.

Note. The peak energies are reproducible to about ±0.01 eV; the absolute accuracy of our measurements is estimated to be ±0.02 eV.

TABLE 2. ASSIGNMENTS OF THE VIBRATIONAL STRUCTURE IN THE ^2B_u BAND OF THE PHOTOELECTRON SPECTRA OF $C_2H_4^+$ AND $C_2D_4^+$ (cm^{-1})

	$C_2H_4^+$	$C_2D_4^+$	C_2H_4	C_2D_4
C—C stretch ν_2	1230 ± 30	1200 ± 30	1623†	1515†
CH_2 twist $2\nu_4$	400 ± 30	230 ± 30	472‡	282†
HCH scissors ν_3	1450 ± 100	1100 ± 100	1342†	981†

† Ground state. ‡ Twisted first Rydberg state.

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Shavitt 1968). Although the structure is observed on both bands it is complex and not completely resolved. A consideration of the orbitals involved indicates that it is quite probable all three totally symmetric vibrations ν_1, ν_2, and ν_3 could be active in both bands; the present results do not contradict the theoretical assignments.

The fourth band is associated with an orbital which is both C—C and C—H bonding. The ethylene photoelectron spectrum appears as a well resolved progression, with a spacing of about 1200 cm^{-1}. The ethylene-d$_4$ photoelectron spectrum, however, shows only three resolved peaks, with a spacing of about 930 cm^{-1}.

Consideration of the orbitals involved and comparison of the bands for the two isotopic species leads to the conclusion that the structure is predominantly due to ν_2 and ν_3, not ν_1, as previously suggested by Baker *et al.* (1968). We consider a change in ν_1 from about 3000 cm^{-1} in the neutral molecule to 1200 cm^{-1} in the ion to be most unlikely. In the $C_2H_4^+$ ion ν_2 and ν_3 are approximately equal and have the value 1200 cm^{-1}, hence reinforcing each other. In the $C_2D_4^+$ ion ν_3 is assigned the value of 930 cm^{-1} and ν_2 1110 cm^{-1}, which would account for the indistinct nature of the spectrum after the first three peaks. These values are also consistent with the Teller–Redlich product rule, with values for ν_1 of 2500 cm^{-1} for ethylene$^+$ and 2000 cm^{-1} for ethylene-d$_4^+$.

Ammonia and ammonia-d$_3$

Our previously reported spectrum of NH_3 (Frost *et al.* 1967*b*), obtained with a retarding grid instrument, exhibited only steps corresponding to ionization from the $(a_1^*)^2$ and $(e)^4$ orbitals, no vibrational structure being resolved. In the spectrum of NH_3 obtained with the new 180° spectrometer (see figure 4) vibrational structure for the $^2A_1$ state is clearly seen up to $v = 15$. This spectrum is similar to that reported by Price (1968) though our resolution seems to be a little better. A better spectrum was obtained using a neon discharge as the radiation source which produces predominantly 736 and 744 Å (16.83 and 16.65 eV). The doublet spacing is approximately equal to the NH_3^+ vibrational spacing for this state (see table 3) and so the only effect is a slight broadening of the peaks. The corresponding spectrum for ammonia-d$_3$ is shown in figure 5.

Table 3. Ionization potentials (eV) for the $^2A_1$ state of NH_3^+

$^2A_1$ vib level	NH_3	ND_3	$^2A_1$ vib level	NH_3	ND_3
0	10.14	(10.17)	9	11.27	11.00
1	10.26	10.26	10	11.40	11.10
2	10.37	10.35	11	11.53	11.19
3	10.49	10.44	12	11.67	11.30
4	10.62	10.53	13	11.81	11.40
5	10.75	10.62	14	11.95	11.50
6	10.87	10.71	15	12.08	11.61
7	11.00	10.81	16		11.70
8	11.14	10.90	17		11.81
			18		11.91

Removal of a lone pair electron is expected to produce the ion in a planar $^2A_1$ configuration, and the observed vibrational sequence is ascribed to ν_2 (inversion). From consideration of the energy corresponding to the envelope maximum (Smith & Warsop 1968) and comparison with the electronic spectra (Walsh & Warsop 1961) the first observed peak in the NH_3^+ photoelectron spectrum is assigned to the $0 \leftarrow 0$ transition. However, for ND_3 similar considerations indicate that the first observed photoelectron transition is associated with the $1 \leftarrow 0$ vibronic process.

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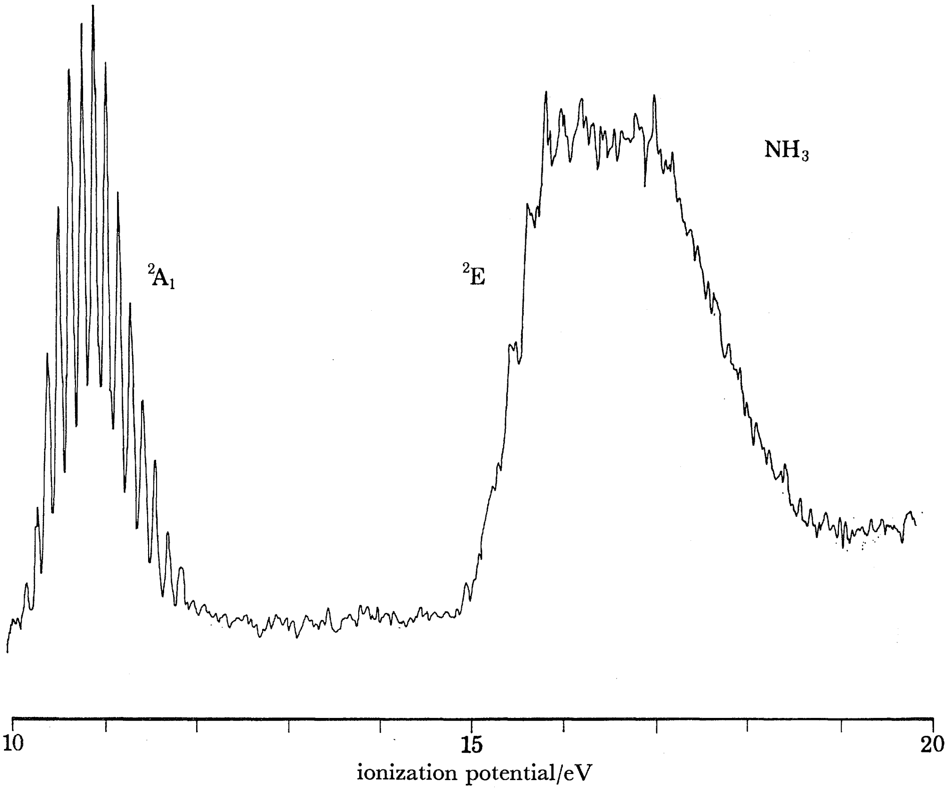

FIGURE 4. Photoelectron spectrum from ammonia obtained using the 584 Å helium resonance line.

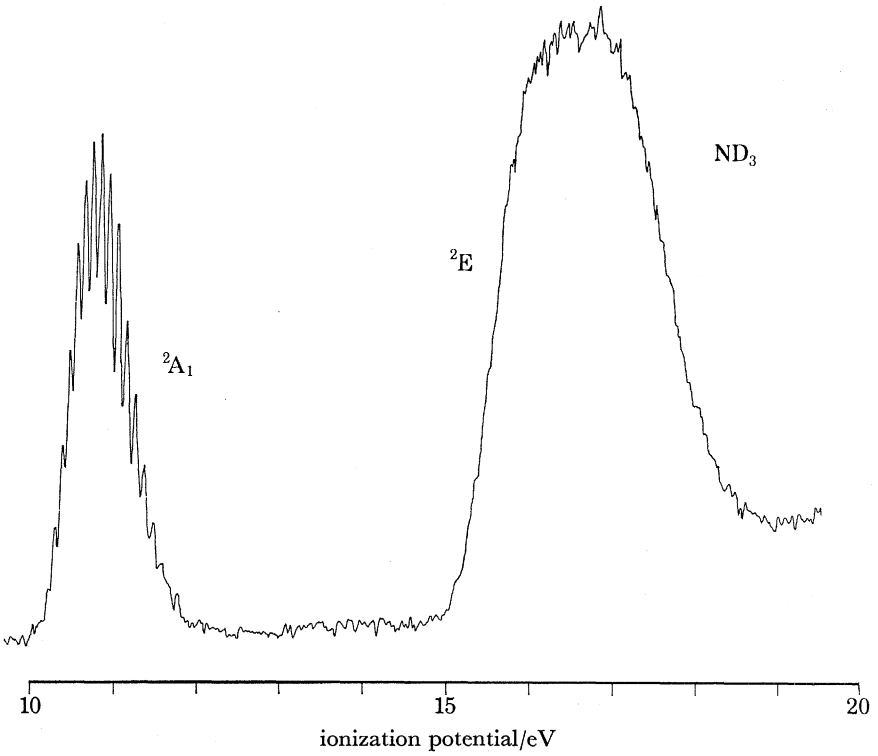

FIGURE 5. Photoelectron spectrum of ammonia-d$_3$ obtained using the 584 Å helium resonance line.

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Therefore, the observed ionization potential of 10.26 eV is 0.09 eV higher than the adiabatic value.

The ionization potential leading to the formation of the ion in its ${}^2E_1$ state was found to be 14.92 and 15.15 eV for NH_3 and ND_3 respectively.

Oxygen

The neon 736–744 Å photoelectron spectrum for oxygen is shown in figure 6. We see three groups of vibrational levels lying between 12 and 16 eV, and that the spacing decreases continuously (0.25 to 0.16 eV at $v = 20$ to 21) suggests they all belong to the same vibronic series associated with the $O_2^+\,{}^2\Pi_g$ ground state. These observations are similar to those reported by Natalis & Collin (1968) and by Price (1968), though here again the bands in our spectrum are better resolved and we observe more transitions.

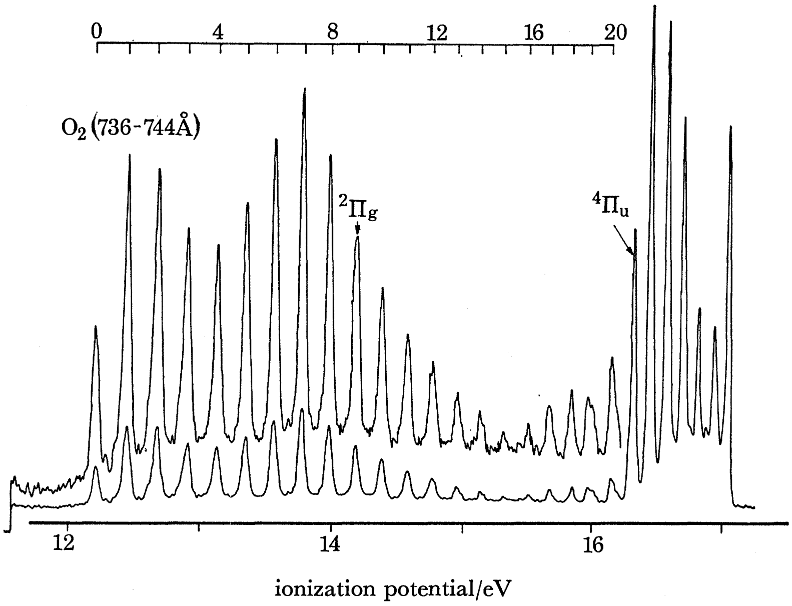

FIGURE 6. Photoelectron spectrum from oxygen obtained using the 736/744 Å doublet of neon.

Using the 584 Å helium resonance line, we see only the levels $v = 1$ to 4 and direct application of the Franck–Condon principle cannot explain the appearance of $v = 5$ to 21. The doublet nature of the neon lamp does not make the peaks noticeably assymmetric since the 736 Å line is about six times more intense than the 744 Å line, and also the vibrational spacing is comparable to the neon doublet separation. Above $v = 21$ the vibrational progression for $O_2^+\,{}^4\Pi_u$ appears (0 to 1 spacing 0.13 eV).

From photoionization studies on oxygen (Cook & Ching 1967) it is evident that the neon 734, 744 Å doublet falls in a region where autoionization is occurring and herein lies the explanation of the observed effects. Autoionization from Rydberg bands at these wavelengths has also been suggested as a possible source of the anomalous and vibrational intensities by Natalis & Collin (1968) and by Price (1968).

The proposed mechanism whereby the three groups of vibrational bands observed in the ${}^2\Pi_g$ state may occur is illustrated in figure 7. The first group is obviously formed by normal Franck–Condon transitions to the first five vibrational levels of $O_2^+({}^2\Pi_g)$, and are, of course, the only ones observed when the 584 Å helium line is used as a source of radiation. To explain

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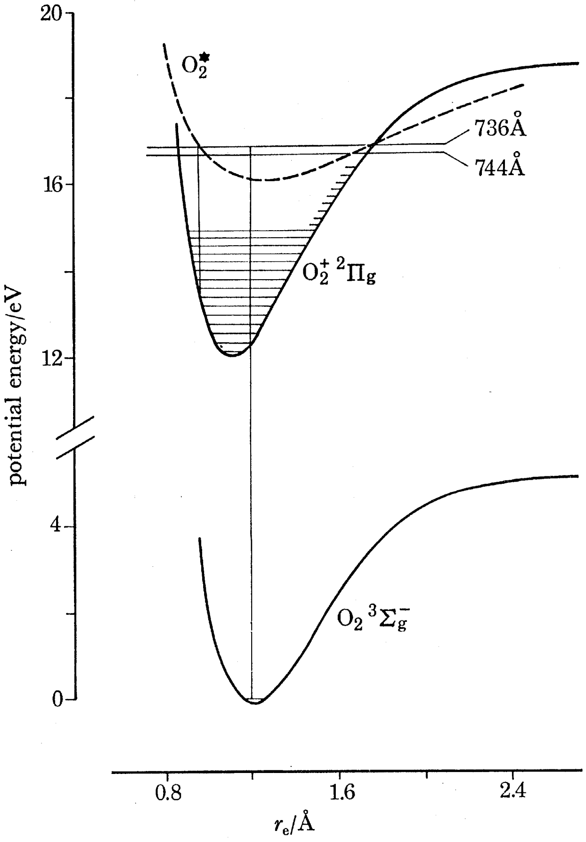

FIGURE 7. Diagram to illustrate possible origin of observed photoelectron spectrum from oxygen with 736/744 Å neon doublet.

the other bands observed we assume the existence of an excited state of oxygen to which Rydberg transitions occur and for which there is an accidental resonance with vibrational levels and the exciting radiation from the neon resonance lamp. There will then be an anomalously large transition moment for this state. Autoionization may then occur and if the lifetime of the postulated state is longer than usual it is possible to explain the occurrence of the second and third group of vibrational levels. Transitions from this autoionizing Rydberg state to the ground state $^2\Pi_g$ of the molecular ion from the two extremes of the nuclear motion of the newly postulated state could produce the two additional sets of vibrational bands observed.

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