

The Photoionization of Molecules in the Vacuum Ultraviolet

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A method of measuring thresholds for photoionization of molecules, corresponding to the first ionization potential, is described. The method is applied to several different molecules (O_2 , NO , NH_3 , SO_2 , C_2H_4 , CH_3I , CH_3OH , C_2H_5Br). The first ionization potentials obtained are compared with those measured by other methods, e.g., electron impact and spectroscopic. The photoionization method gives greater precision than the electron impact method and is applicable to cases where the spectroscopic method fails.

THE usual methods of determining ionization potentials of molecules are by electron impact and spectroscopically by the convergence limit of Rydberg series. We report here a somewhat different, and perhaps more direct, method for measuring the first ionization potential of molecules by determining the threshold for photoionization. Since the ionization potentials of many molecules are greater than 6 ev, the photoionization measurements must be made in the vacuum ultraviolet.

The apparatus used for these measurements has been described elsewhere.^{1,2} Briefly, monochromatic radiation (0.85A band width) from a Baird 1-meter vacuum monochromator was allowed to pass through a photoionization cell located behind the exit slit (0.05 mm wide) of the monochromator. Parallel plate (Pt) elec-

trodes in the cell were used to collect the ions produced by photoionization. To insure collection of all ions, the voltage applied (about 10 volts) to the electrodes was set a few volts above saturation, end plates used, and the monochromatic beam centrally located in the volume element defined by the electrodes. The ion current was measured with a Beckman micro-microammeter (10^{-8} – 10^{-14} amp) and recorded on a Speedomax recorder. The cell was in communication with a gas filling system, thus allowing the cell to be readily filled with the purified gas or vapor at any desired pressure. By scanning (20A per minute) the spectral region near the threshold, the ion current is recorded and the wavelength at which the first ions appear, followed by a sharp increase in ion current, is determined with considerable accuracy. Photoelectric effects due to scat-

TABLE I. Observed ionization potentials compared with those obtained by other methods.

Molecule	Threshold (A)	Ionization potential ev		Method
		Our values	Previously reported values	
O_2	1029	12.04 ± 0.01	12.2 ± 0.1	cycle ^b
			12.1 ± 0.2	electron impact ^c
NO	1343	9.23 ± 0.02^a	9.4 ± 0.2	electron impact ^c
NH_3	1223	10.13 ± 0.02	10.5 ± 0.1	electron impact ^d
SO_2	998	12.42 ± 0.06	12.05 ± 0.05	rough extrapolation of Rydberg series ^e
			13.3 ± 0.3	electron impact ^f
C_2H_4	1184	10.47 ± 0.02	10.45 ± 0.03	Rydberg series ^g
			10.80 ± 0.05	electron impact ^h
			10.62	electron impact ⁱ
CH_3I	1305	9.497 ± 0.007	9.490 ± 0.002	Rydberg series ^j
	1349	9.19 ± 0.02	9.1 ± 0.25	electron impact ^k
CH_3OH	1178	10.52 ± 0.03	10.8	electron impact ^l (quoted by Price)
C_2H_5Br	1211	10.24 ± 0.02	10.24 ± 0.02	by comparison with CH_3Br Rydberg series ^m
	1255	9.88 ± 0.03	10.0 ± 0.25	electron impact ^k

^a See reference 2.

^b R. S. Mulliken and D. S. Stevens, *Phys. Rev.* **44**, 720 (1933).

^c H. D. Hagstrum, *Revs. Modern Phys.* **23**, 185 (1951).

^d Mann, Hustrulid, and Tate, *Phys. Rev.* **58**, 340 (1940).

^e W. C. Price and D. M. Simpson, *Proc. Roy. Soc. (London)* **A165**, 272 (1938).

^f H. D. Smyth and D. W. Mueller, *Phys. Rev.* **43**, 121 (1933).

^g W. C. Price and W. T. Tuttle, *Proc. Roy. Soc. (London)* **A174**, 207 (1940).

^h Kusch, Hustrulid, and Tate, *Phys. Rev.* **52**, 843 (1937).

ⁱ R. E. Honig, *J. Chem. Phys.* **16**, 105 (1948).

^j W. C. Price, *J. Chem. Phys.* **4**, 539 (1936).

^k T. N. Jewitt, *Phys. Rev.* **46**, 616 (1934).

^l W. C. Price, *Chem. Revs.* **41**, 257 (1947).

^m W. C. Price, *J. Chem. Phys.* **4**, 547 (1936).

¹ Watanabe, Inn, and Zelikoff, *J. Chem. Phys.* (to be published).

² Watanabe, Marmo, and Inn, *Phys. Rev.* **90**, 155 (1953).

tered and multiply-reflected radiation at the electrodes were exceedingly small compared to the ion currents measured.

In order to compare this method of determining ionization potentials with those mentioned above, a number of molecules were studied and the results are shown in Table I. The accuracy of the values obtained is indicated in the third column, which represents the degree of uncertainty in determining the exact wavelength at which the first ions appear in the measurement of the photoionization current. It is seen that, in general, there is good agreement with those reported by other investigators, exceptionally so with those determined by Rydberg series methods. Since electron impact values essentially correspond to vertical processes, it is not surprising that our values are lower and agree better with the more correct spectroscopic values corresponding to adiabatic processes.

An unusual effect was noted in the case of CH_3I and $\text{C}_2\text{H}_5\text{Br}$. There appeared to be a second threshold at

longer wavelengths, although the cutoff was much less pronounced and sharp as compared to the shorter wavelength threshold. The ion current was also much smaller than that produced at the shorter wavelength threshold. Two possible explanations for this effect may be given: (1) photoionization of dissociation products which may have lower ionization potentials; or (2) ionization due to transitions $v'' > 0$ of the ground state of the normal molecule to the $v' = 0$ of the ground state of the ionized molecule.

In the case of O_2 , NO , NH_3 , and CH_3OH , in which no Rydberg series has been observed with any degree of success, it can be seen that the present method is particularly adapted for obtaining accurate measurements of the ionization potential. In fact, this method should be generally applicable for determining first ionization potentials of a wide variety of molecules and in addition for determining molecular ionization cross sections.²

Accurate Determinations of Nuclear Reaction Energies*

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A precise magnetic spectrometer of the annular type is described; the focusing properties and line shapes are analyzed. The use of the instrument to measure absolute particle momenta in terms of the proton magnetic moment precessional frequency and a standard length is presented for three nuclear transmutations and for the determination of the energy necessary to excite a state in Ne^{20} . The Q values obtained are: $\text{C}^{12}(d, p)\text{C}^{13}$, $Q = 2.722 \pm 0.004$ Mev; $\text{O}^{16}(d, \alpha)\text{N}^{14}$, $Q = 3.119 \pm 0.005$ Mev; and $\text{Li}^7(p, \alpha)\text{He}^4$, $Q = 17.344 \pm 0.013$ Mev. The energy at a resonance in the reaction $\text{F}^{19}(p, \alpha\gamma)\text{O}^{16}$ was determined to be 872.5 ± 1.8 kev.

I. INTRODUCTION

ACCURATE determinations of the energies of evolution of nuclear transmutations yielding heavy particles have been performed in a number of laboratories in recent years; modern techniques have allowed the construction of very precise magnetic and electrostatic spectrometers,¹ and one result of the measurements performed with these instruments has been the preparation of accurate tables of atomic masses for the light elements.² A precise knowledge of these masses is desirable so that theories of binding energies of nuclei may be constructed, and to allow the prediction of particle energies and the energies of excitation of nuclei. Atomic masses are also determined

with great accuracy by the methods of mass spectrometry; however, it has been pointed out that the nuclear and mass spectroscopic methods have not always yielded mass values that agreed within the assigned errors for the measurements.² Since either or both methods could have small errors that might account for this disagreement, it seemed desirable to attempt an accurate, absolute, and independent redetermination of the nuclear data. This paper will describe the techniques developed to accomplish the determinations and will present some of the results.

In reviewing the possibilities of obtaining nuclear disintegration data of greater absolute accuracy than in earlier determinations, five possible sources of error in the previous determinations were noted and an attempt has been made to diminish the magnitude of these possible errors. (1) Most measurements of nuclear transmutation energies have been performed on particles emitted in directions θ that were not optimum with respect to the direction of bombardment. The classical expression for the energy of evolution, Q , of a nuclear

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¹ Buechner, Strait, Stergiopoulos, and Sperduto, *Phys. Rev.* **74**, 1569 (1948); Snyder, Ruben, Fowler, and Lauritsen, *Rev. Sci. Instr.* **21**, 852 (1950); Brown, Craig, and Williamson, *Rev. Sci. Instr.* **22**, 952 (1951).

² Li, Whaling, Fowler, and Lauritsen, *Phys. Rev.* **83**, 512 (1951).