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PHOTOELECTRON SPECTROSCOPY OF SUPersonic MOLECULAR BEAMS

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We report the development of an instrument for gas-phase ultraviolet photoelectron spectroscopy which opens several new areas for study through use of the supersonic molecular beam technique. The key features in which we have sought an improvement on earlier spectrometer designs are (1) the optimization of electron energy resolution and sensitivity, (2) vacuum isolation, and (3) the capability for mass spectrometric analysis. Our principal interests are in the high resolution spectroscopy of small molecules and in studies of weakly bound complexes formed under collisionless conditions.

As shown in Fig. 1 the apparatus is essentially a molecular beam chamber with allowance for access by a beam source, an electron energy analyzer, and a quadrupole mass spectrometer. These three plug-in units are equipped with individual differential pumping systems. The photon source is a rare-gas resonance lamp which may be directed toward the molecular beam either 90° or 54.7° from the direction of electron collection. Electrons which pass through entrance aperture are transported by a series of electrostatic lenses to a 90° spherical sector pre-analyzer ($R_0 = 3.8$ cm) and then on to a 180° hemispherical analyzer ($R_0 = 10.2$ cm). The detector consists of a microchannel plate electron multiplier (40 mm diam.) with a resistive-anode position encoder. The function of the pre-analyzer is to improve the signal-to-noise ratio by reducing the background of scattered electrons incident upon the microchannel plate. The electron optical system is designed such that the energy bandpass (FWHM) leaving the pre-analyzer just fills the energy window presented by the multichannel detector. The multichannel capability of this analyzer is very advantageous for working with the rather low number density ($\ll 10^{13}$ cm$^{-3}$) of molecular beam samples, since the data collection rate is improved by more than an order of magnitude over single channel operation. To avoid problems due to stray magnetic fields, the electron flight path is shielded by two continuous layers of mu-metal, and the electron optics are constructed entirely of non-permeable...
materials (primarily aluminum, molybdenum, and copper). The 180° analyzer and detector are separated from the ionization region by two stages of differential pumping and are maintained in the 10⁻⁹ Torr range during operation. This vacuum isolation will facilitate the study of corrosive or condensible materials as well as atmospheric gases. The quadrupole mass spectrometer is used for in situ analysis of the photoions, allowing the formation of clusters or transients in the beam to be monitored.

Recently it has been shown that the use of a supersonic jet source can reduce appreciably the Doppler and rotational broadening that usually limit the ultimate resolution in PES.¹ Our apparatus should permit high resolution studies to be performed with good efficiency. Progress is also expected in the application of PES to weakly-bound complexes, a field which has only recently been opened.²⁻⁴ We are presently carrying out the first tests of this instrument, and we anticipate reporting our initial experimental results.

REFERENCES
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Figure 1. Schematic diagram of the apparatus: (1) beam source, (2) beam catcher, (3) pass energy select lens, (4) field lens, (5) kinetic energy scan lens, (6) deflectors, (7) 90° spherical sector pre-analyzer, (8) conductance barrier, (9) 16:1 decelerator lens, (10) 180° hemispherical analyzer, (11) multichannel detector, (12) ion extraction lenses, (13) quadrupole mass spectrometer, (14) differential pumping. The photon beam intersects the molecular beam perpendicular to the plane of the drawing. Not shown are two layers of mu-metal which surround the electron flight path.
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