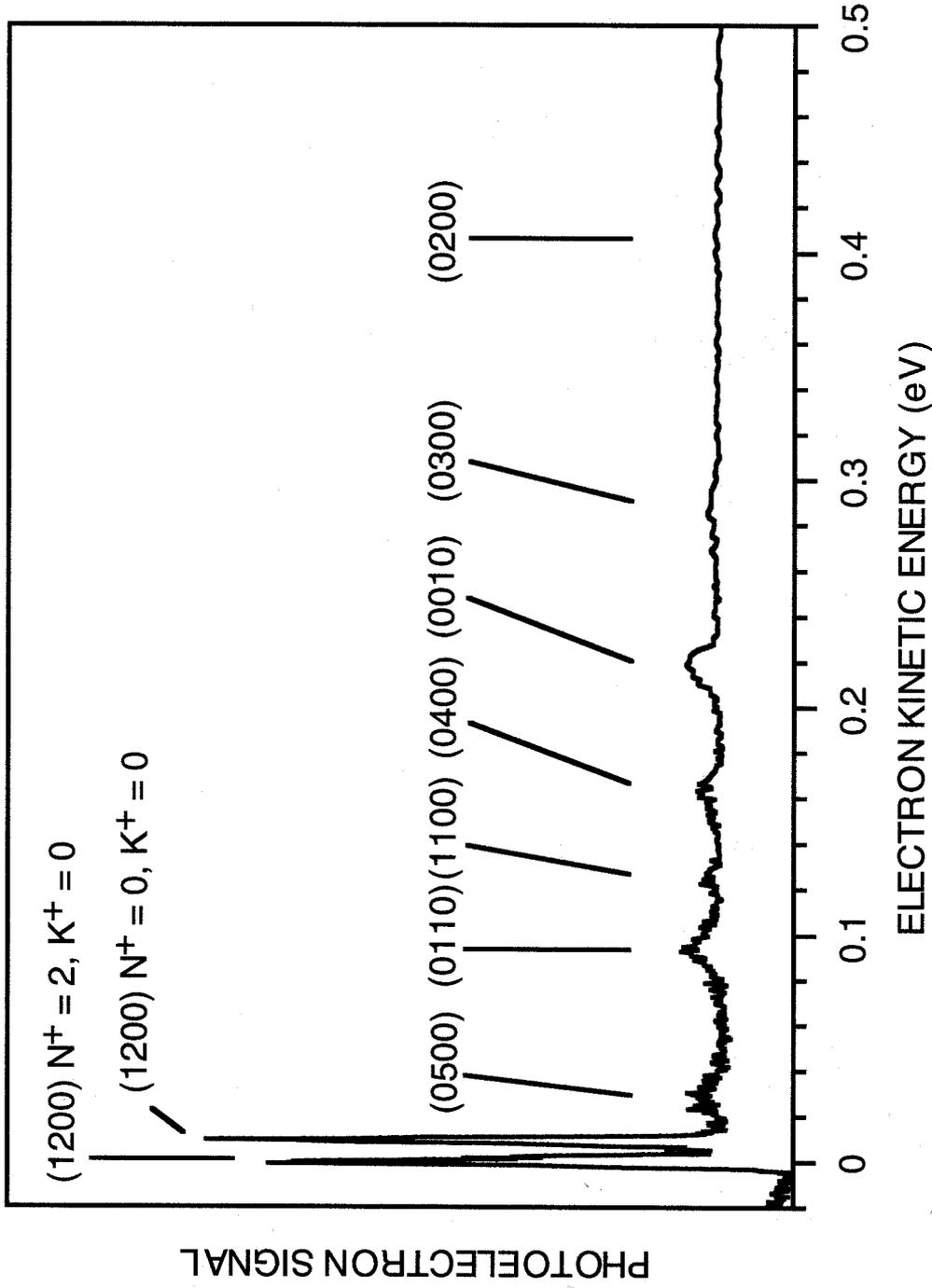


VIBRATIONAL MODE-DEPENDENT IONIZATION PROCESSES

The study of molecular photoionization and photodissociation dynamics provides insight into the intramolecular mechanisms by which energy and angular momentum are exchanged and redistributed among the internal degrees of freedom of highly excited molecules and, more specifically, into the mechanisms that determine the decay pathways and resulting product-state distributions for the excited molecules. These mechanisms lie at the heart of one of the principal subjects of chemistry, that is, understanding and controlling the factors that govern the making and breaking of chemical bonds. Vibrational autoionization is a particularly interesting form of intramolecular energy transfer, as it corresponds to the decay of highly excited, quasi-bound states lying above the ionization threshold into the ionization continuum through the conversion of vibrational energy of the molecule into electronic (and subsequently translational) energy of the ejected electron.

Recently, the vibrational mode dependence of this process has been studied for highly excited states of the ammonia molecule, NH_3 . Specifically, high-resolution photoelectron spectroscopy has been used to determine whether the symmetric stretching vibration or the umbrella bending vibration drives the ionization process more efficiently. Interestingly, autoionization via the umbrella vibration is found to be approximately 20 times faster than via the symmetric stretching vibration. A qualitative model for this process explains these results based on how the electronic structure of the molecule changes along the two vibrational coordinates. This work is currently being extended to include the two other vibrational modes in NH_3 , which correspond to the asymmetric stretch and asymmetric bend. The new results should provide a rigorous test of the qualitative model. If successful, this model is expected to have applicability in a broad range of molecules.

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The photoelectron spectrum obtained by exciting an $1d$ Rydberg state converging to the (1300) vibrational level of the ground state of the ammonia ion. The (1300) level corresponds to one quantum in the symmetric stretch and three quanta in the umbrella bend. The photoelectron spectrum shows that the loss of one quantum in the symmetric stretch, which produces the (0300) level of the ion, is a very weak process, while the loss of one quantum in the umbrella mode, which produces the (1200) level of the ion, is the dominant process. The resolution is sufficient to resolve rotational structure in the (1200) level of the ion, which provides additional information on the autoionization mechanism. The remaining photoelectron peaks are produced through a more complex ionization process.