

EXPERIMENTAL REMPI STUDIES OF SMALL MOLECULES*

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Resonance Enhanced Multiphoton Ionization (REMPI) utilizes tunable dye lasers to ionize an atom or molecule by first preparing an excited state by multiphoton absorption and then ionizing that state before it can decay. This process is highly selective with respect to both the initial and resonant intermediate states of the target, and it can be extremely sensitive. In addition, the products of the REMPI process can be detected as needed by analyzing the resulting electrons, ions, fluorescence, or by additional REMPI. This points to a number of exciting opportunities for both basic and applied science. On the applied side, REMPI has great potential as an ultrasensitive, highly selective detector for trace, reactive, or transient species. On the basic side, REMPI affords an unprecedented means of exploring excited state physics and chemistry at the quantum-state-specific level. We shall give an overview together with examples of current studies of excited molecular states to illustrate the principles of and prospects for REMPI.

I. INTRODUCTION

Rapid advances in laser and detector technologies are making it possible to investigate molecular photophysics and photochemistry in powerful new ways. For example, resonantly enhanced multiphoton ionization (REMPI) measurements, in which the total (or the mass selected) ion current is monitored as a function of laser wavelength, have yielded extensive and often novel information on the spectroscopy of the resonant intermediate states (1). More recently, several groups have begun to monitor REMPI by measuring the kinetic energy distribution of ejected electrons (2,3), thus directly probing the photoionization dynamics of excited states. These and other experimental approaches, outlined below, are motivated by the prospect of investigating the spectroscopy and dynamics of excited molecular states at the quantum-state-specific level. Moreover, the resulting ability to selectively probe molecular excitation and decay has direct bearing on a variety of applied fields, e.g. ultrasensitive detection of unstable, reactive, or trace species, the characterization of the physics and chemistry of excited states that mediate the effects of ionizing radiation on matter, isotope separation, laser-modified chemistry, modeling of plasmas and the physics and chemistry of the atmosphere in normal and disturbed states.

To illustrate the potential of REMPI, we will outline several different types of experiments that can be carried out using the two-color REMPI excitation processes shown schematically in Figure 1. In Figure 1a, two photons from a "pump" laser with frequency $h\nu_1$ are used to excite an individual rotational (not shown) and vibrational level of an excited electronic state AB^* . An independently tunable "probe" laser of frequency $h\nu_2$ is

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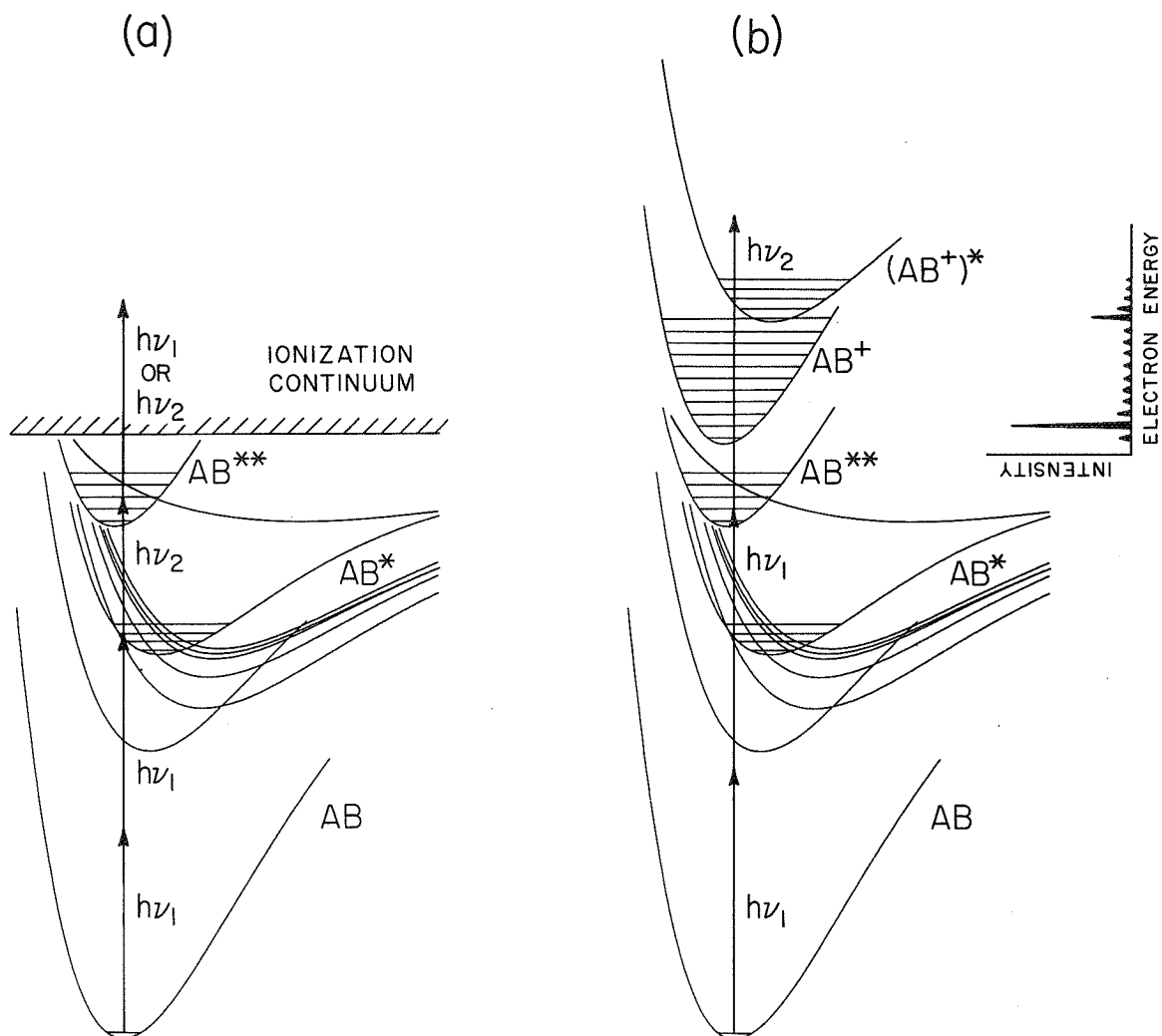


Fig. 1. Schematic potential energy diagram showing two different REMPI processes in a diatomic molecule.

used to further excite the AB^* level to the manifold of rotational-vibrational levels of a higher excited state AB^{**} . A third photon of frequency $h\nu_1$ or $h\nu_2$ is used to ionize AB^{**} . In this case, one is interested in the $AB^* \rightarrow AB^{**}$ transition rather than the ionization step, so the continuum is represented simply by a structureless hatched area. In Figure 1b, a similar process is indicated; however, in this case, the state AB^{**} is produced by two photons of the pump laser, with the probe laser accessing the ionization continuum directly. Here, one is interested in the ionization step itself, and so the accessible ionic states AB^+ and $(AB^+)^*$ are shown explicitly.

The resonant multicolor excitation schemes represented schematically in Figure 1 permit us to address many problems in molecular science which were either very difficult or unimaginable with conventional excitation sources. These include the following. (a) By varying $h\nu_2$ (in Figure 1a) and detecting the total (or mass selected) ion current as a function of wavelength, one

performs optical-optical double resonance (OODR) spectroscopy. This generates spectroscopic information on AB^{**} which typically lies in the vacuum ultraviolet (VUV) with single photon sources, but in the visible or ultraviolet with multiphoton sources. This produces high resolution spectroscopic information without the need of a large vacuum spectrograph. More importantly, the $h\nu_2$ transition originates from a single rotational level of AB^* , which greatly simplifies the spectrum. Use of OODR techniques also enables the direct study of states that are dipole forbidden in single photon excitation. (b) If the excited state AB^{**} is predissociated, e.g., by the repulsive curve in Figure 1, it is possible to probe in detail the mechanisms of the dissociation process by analyzing both the internal energy distribution of the photofragments and the time dependence of their formation. In addition, photodissociation often is one of the simplest and most convenient methods of producing open shell atoms, free radicals or transient species for further spectroscopic study. (c) Measurement of the photoelectron energy distribution (indicated by the inset in Figure 1b) will give the relative probabilities of producing alternative ionic states and, thus will directly reflect the photoionization dynamics of individual excited quantum states. It also will be possible to determine photoelectron branching ratios and angular distributions at various points within an autoionizing resonance, which will be an extremely sensitive probe of the interactions between the discrete state and the various ionization continua. At present, such measurements are being performed using synchrotron radiation light sources with modest wavelength resolution ($\sim 0.2-0.5 \text{ \AA}$); however, this wavelength resolution is rarely sufficient to sample different regions within a single autoionizing resonance. (d) Since the ionization step in Figure 1b is performed with a visible or UV wavelength, simple rotation of a retardation plate will produce a photoelectron angular distribution, which accesses further dynamical information and also reflects the orientation of the excited state AB^{**} , resulting from the multiphoton excitation process. (e) Preparation of an excited state AB^{**} , followed by a delayed laser probe can monitor the time evolution of intramolecular rearrangement and/or decay processes. In molecules more complicated than that indicated in Figure 1, this procedure can monitor the time evolution of vibrational energy redistribution. In this case, picosecond lasers would be required to capture the normally very fast internal rearrangement. Use of a delayed probe beam can also be used to characterize collisional effects on a prepared state. (f) Using the high degree of selectivity, and hence, sensitivity of either excitation mechanism in Figure 1, it is possible to directly probe free radicals, clusters, ions and other transient species which are formed as minor components in complex mixtures. (g) Many possible chemical uses of the general scheme in Figure 1 can also be readily seen. For instance, by suitable selection of AB^{**} in Figure 1b, it is possible to produce AB^+ or AB^{+*} in particular vibrational and rotational quantum states in order to study the dependence of subsequent chemical transformations on varying degrees of internal energy in different electronic or nuclear modes. Also, by using the selectivity of the excitation process, it is possible to monitor the reactants and products of elementary chemical reactions at the quantum-state-specific level.

This list of possibilities is not exhaustive, but is ample to show the great scientific potential of REMPI. In what follows, we will present selected examples of REMPI studies in somewhat more detail.

II. PHOTOIONIZATION DYNAMICS OF EXCITED MOLECULAR STATES

A major area of investigation using REMPI-PES is the study of branching ratios following photoionization of excited molecular states. This is a virtually unexplored area, since conventional single photon PES studies have been almost completely limited to ground state ionization. Because of its importance as a theoretically tractable molecule, H_2 has received considerable attention during the past few years, and REMPI-PES studies have been reported for excitation via the $B \ ^1\Sigma_u^+$ (4,5), $B' \ ^1\Sigma_u^+$ (6), $C \ ^1\Pi_u$ (7-9), $D \ ^1\Pi_u$ (6), and $E, F \ ^1\Sigma_g^+$ (10,11) resonant intermediate states. As an example, Figure 2 shows the REMPI-PES obtained along the laser polarization axis ($\theta = 0^\circ$) at the wavelengths of the resonant three-photon $C \ ^1\Pi_u, v' = 0-4 + X \ ^1\Sigma_g^+, v'' = 0, Q(1)$ transitions (7); angular distributions were determined for the more intense peaks (8). The most striking aspect of the photoelectron spectra is the dominance of the photoelectron peak corresponding to the $v^+(X \ ^2\Sigma_g^+) = v'(C \ ^1\Pi_u)$ transitions. In addition, the weaker peaks with the greatest intensity are those adjacent to the $v^+ = v'$ peak. This agrees with expectations based on Franck-Condon factor calculations; however, while the qualitative agreement was found to be very good, the quantitative agreement was poor (7). For example, in the spectrum excited via $C \ ^1\Pi_u, v' = 4$, the $v^+ = 3, 5$, and 6 peaks are too large by factors of 3, 2, and 23, respectively, and the intensity of the $v^+ = 4$ peak accounts for only 43% of the total, rather than the predicted 90%. The most probable reasons for this behavior are the energy and the internuclear distance dependence of the electronic transition moment or the presence of autoionizing states (including doubly excited autoionizing states) in the ionization continuum.

The detail of these and other experimental results on H_2 and other diatomic molecules such as NO (12,13) permits a direct comparison with theory, which allows an assessment of the accuracy of various theoretical models. However, a theoretical analysis of molecular REMPI processes is complicated for two reasons -- (1) the inherent nonlinearity of multiphoton absorption introduces dynamical effects such as saturation, a.c. Stark shifts, alignment of excited states, and the sensitivity of the REMPI probability to the spatial and temporal characteristics of the laser, and (2) the molecular aspects of the problem introduce complications, particularly the multicenter nature of the molecular field and the interaction among the rotational, vibrational, and electronic states. Recently, Dixit et al. (14-20) have begun a theoretical program to analyze REMPI processes in diatomic molecules. Their approach is to calculate the molecular parameters (transition moments, photoionization cross sections, and scattering phase shifts) at an *ab initio* level and then to carry out the REMPI dynamics. Their calculation (14) of the branching ratios and angular distributions for the (3+1) REMPI of the $C \ ^1\Pi_u$ state of H_2 were in good agreement with the experimental results for the lower vibrational levels, although significant differences were observed for the higher vibrational levels.

Thus, the field of excited state photoionization dynamics is at an early and most interesting stage of development, the first detailed experiments and calculations having been performed very recently. The continuation and expansion of such studies promises to provide a much clearer understanding of REMPI processes.

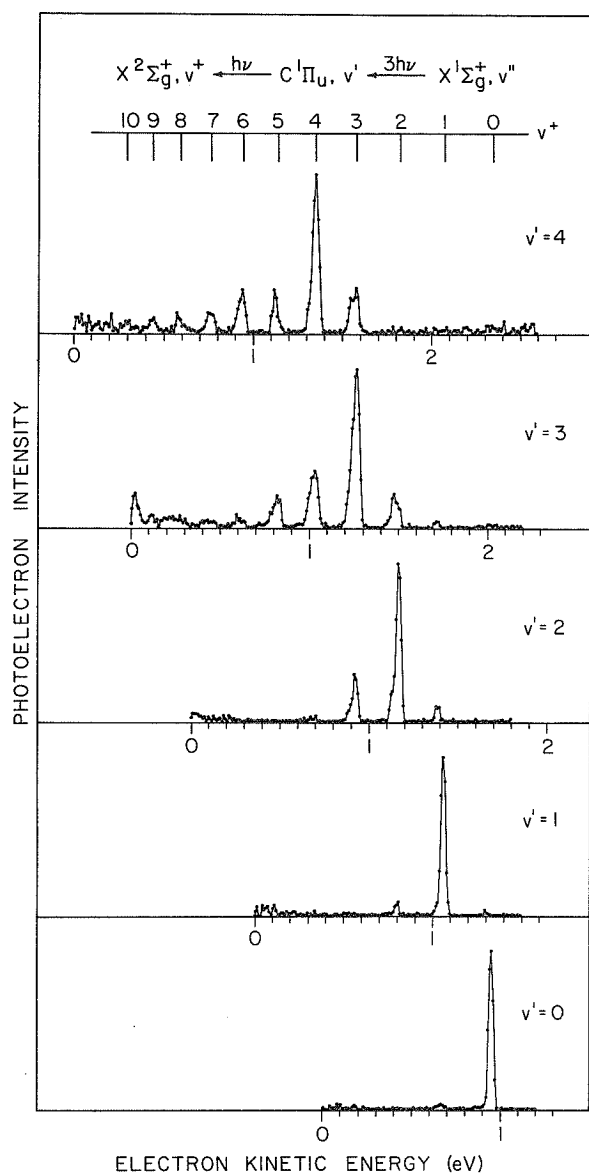


Fig. 2. REMPI-PES of H_2 determined at the wavelengths of the resonant three photon $C^1\Pi_u, v' = 0 - 4 \leftarrow X^1\Sigma_g^+, v'' = 0, Q(1)$ transitions. Note the dominance of the photoelectron peak corresponding to the $v^+(X^2\Sigma_g^+) = v'(C^1\Pi_g)$ ionizing transition.

III. REMPI STUDIES OF OPEN SHELL ATOMS

As mentioned in the Introduction, REMPI provides a powerful means for preparing and studying open-shell atoms, free radicals, and transient species via photodissociation. For illustration, we will briefly discuss some recent work on atomic iodine, although several other atoms (e.g., O, C, S) have already been studied and the technique is thought to be quite broadly applicable. During the past few years, considerable progress has been made in the experimental study of photoionization of halogen atoms (21-25); however, the best resolution attained to date in such experiments ($\sim 20 \text{ cm}^{-1}$) is not sufficient to resolve all of the features of interest. For example, the spectrum of atomic iodine between 1120 Å and 1090 Å contains Rydberg series converging to two ionization limits within this region as well as members of a third Rydberg series converging to a limit at higher energy. Therefore, it is extremely difficult, if not impossible, to sort out the complex structure

(21). For this reason, we investigated the possibility of using laser techniques for the study of this problem. We used two color multiphoton ionization mass spectrometry to determine the spectra of the optically allowed autoionizing states of atomic iodine. In these experiments, the first laser is used to produce atomic iodine by the photodissociation of methyl iodide and to pump the iodine atoms to a low lying $\dots 5p^4 6p$ state via a two photon transition. A second laser is used to probe single photon transitions from these $\dots 5p^4 6p$ states to autoionizing $\dots 5p^4 ns$ and nd Rydberg states converging to the 1D_2 ionization limit. Because a total of three photons is used, this process accesses states of the same parity as those accessed by single photon excitation. However, the resolution in the present experiments is limited only by the linewidth of the laser ($\sim 0.05 - 0.3 \text{ cm}^{-1}$). Thus, it is possible to study the photoionization spectrum of atomic iodine and other open shell atoms with unprecedented detail.

The choice of the resonant intermediate state will determine the manifold of autoionizing states that may be observed. Two primary considerations are useful in deciding which resonant intermediate state should be used. First, transitions that preserve the ion core of the resonant intermediate state are, in general, stronger than those that require a change in the ion core. For example, the transitions $(^1D_2)6p \rightarrow (^1D_2)ns, nd$ are expected to be stronger than the transitions $(^3P_1)6p \rightarrow (^1D_2)ns, nd$. Second, by specifying the values of K and J for the resonant intermediate state, it is possible to limit the range of values of K and J of the autoionizing Rydberg states owing to the angular momentum selection rules.

Spectra were obtained by pumping the two photon transition from the $^2P_{1/2}$ state to the $(^1D_2)6p[3]_{5/2}$ and $(^1D_2)6p[1]_{1/2}$ states and probing transitions to the $(^1D_2)ns$ and nd Rydberg series converging to the 1D_2 ionization limit. The former spectrum displays three sharp series that can be resolved to high principal quantum numbers ($n \sim 35$), while the latter spectrum displays a single sharp series and a single broad series. The symmetry of several of these series was deduced from angular momentum coupling rules. Several recent REMPI-PES studies have shown that ionization into a structureless continuum via an unperturbed Rydberg state usually proceeds by the ejection of the Rydberg electron without a change in the electronic or vibrational state of the ion core (3). Thus, in many instances REMPI can be used as a source of state-selected ions. However, the results can be quite different if the resonant intermediate level is perturbed, because the character of the unperturbed level will then be mixed with that of the perturbing level. If the two interacting levels have different ion cores, the perturbation is revealed in the photoelectron branching ratios following REMPI. In this work, REMPI-PES was used to study a perturbation in the odd parity Rydberg series of atomic iodine and to determine the feasibility of producing state-selected I^+ ions using REMPI. It was shown that, while state selected ions can be produced in some cases, the state selecting capability of REMPI is dramatically reduced for perturbed levels. For example, the photoelectron spectra obtained via the $(^3P_2)nf[3]_{5/2}$ levels show the effect of a perturbation by the $(^3P_0)4f[3]_{5/2}$ level.

As a consequence of the small ionization cross sections of the Rydberg levels in these experiments, two processes were observed that compete with REMPI. The first involves fluorescence of the resonant intermediate level to a lower lying level, which is then ionized with greater efficiency, and the

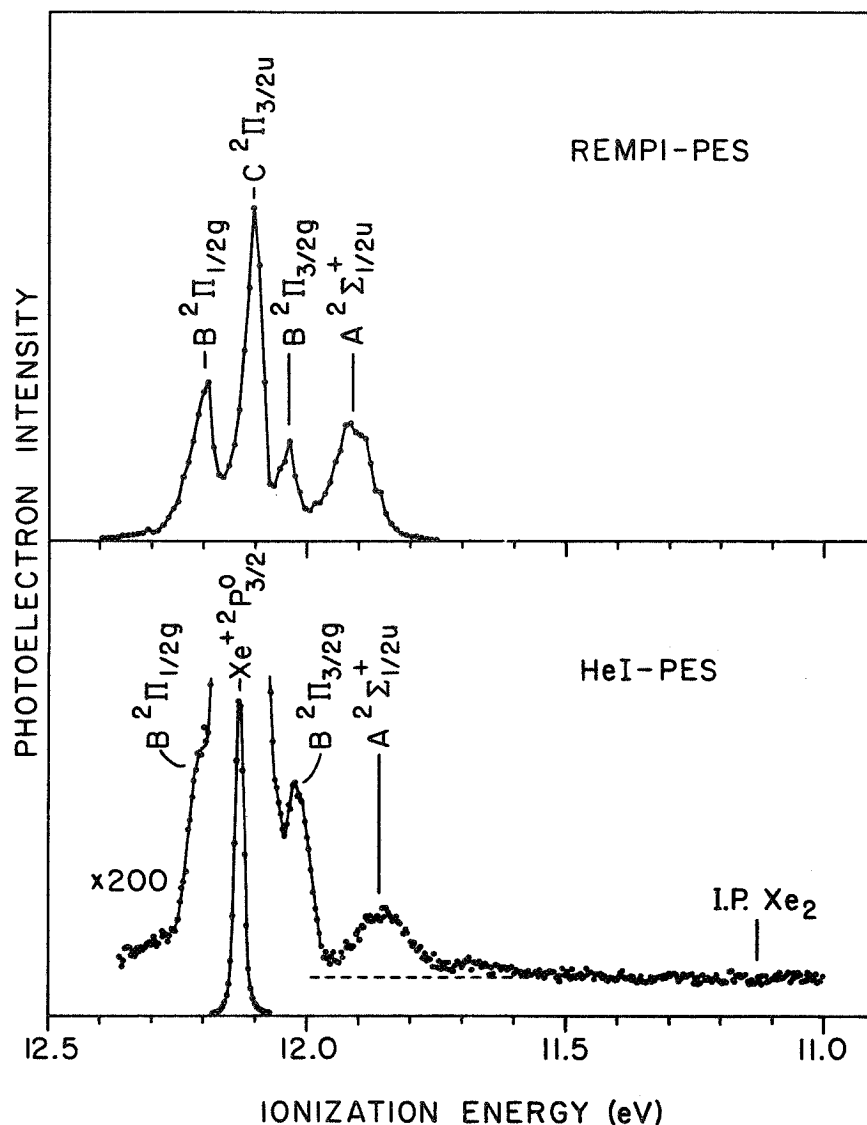


Fig. 3. HeI-PES of Xe_2 (lower trace) and REMPI-PES of Xe_2 determined at the wavelength of the resonant two photon $\text{Xe-Xe}^* 5d[5/2]_g^2, v' = 0 + \text{Xe}_2 X^1\Sigma_g^+, v'' = 0$ transition (upper trace). The spectra are shown in the region of the $\text{Xe}^+ 2P_{3/2}^0$ atomic ionization limit. Note that atomic ionization is more than 100 times as intense as the molecular ionization in the HeI-PES, but that no atomic ionization is observed in the REMPI-PES, because the energy of the Xe_2 resonant intermediate state does not correspond to an energy level of atomic Xe.

second involves energy transfer (either collisional or radiative) between $\text{I}^*2P_{1/2}$ atoms and the Rydberg atoms. Although these two processes would be indistinguishable from direct REMPI using mass spectrometric techniques alone, the use of REMPI-PES allows the separation of the contributions of these different mechanisms and provides a more complete understanding of the overall process.

IV. REMPI STUDIES OF MINOR COMPONENTS

It is also possible to use REMPI-PES to determine the ionic energy levels of species that are present in small concentrations in the presence of a species with an interfering PES. In this case, REMPI is used to selectively ionize the species of interest, while leaving the interfering species unexcited. For example, the photoelectron spectra of the homonuclear rare gas dimers Ar_2 , Kr_2 , and Xe_2 were determined several years ago using conventional HeI PES (26,27). However, since the rare gas dimer is present in concentrations of only a few percent in the supersonic molecular beam, the single photon PES of the rare gas dimers were dominated by photoelectrons from photoionization of the free atom. In the case of Xe_2 , the atomic photoelectron peaks were found to obscure half of expected photoelectron bands; however, the spectra obtained using REMPI-PES are completely free of these atomic photoelectron peaks. Figure 3 shows an example of a HeI-PES and a REMPI-PES of Xe_2 in the region of the $\text{Xe}^+ 2P_{3/2}^0$ ionization threshold. This region of the photoelectron spectrum contains transitions to four molecular states -- the $\text{Xe}_2^+ A 2\Sigma_u^+$, $B 2\Pi_{3/2g}$, $B 2\Pi_{1/2g}$, and $C 2\Pi_{3/2u}$ ionic states. The data of Figure 3 show that in the HeI-PES only two of the molecular bands are clearly observed. In the REMPI-PES, however, all four molecular bands are seen, and there is no evidence of atomic photoelectron peaks. These data can be analyzed to determine detailed information on the potential energy curves of the ionic states.

In the above example, the minor component (Xe_2) in the sample was produced in a supersonic expansion; however, trace species or free radicals can also be produced by the pulsed laser and the REMPI-PES determined in the same laser pulse. Frequently, this is one of the best methods for producing and studying radicals or reactive species.

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