comparison of the predicted and measured angular distributions can then identify the symmetry of the intermediate state. (See, e.g., ref 48–50).

As an example let us consider the shape resonance which occurs in e–H_2 collisions at around 3 eV. The symmetry of this resonance has been predicted to be $^2\Sigma_u^+$,[51] and the angular distribution associated with this symmetry is: $\sigma(\theta) \propto 1 + 2\cos^2\theta$. This prediction has been confirmed by the measurement of the angular distribution of the scattered electrons in the vibrational excitation channel.[52]

Very recently Langendam et al.[53] and Langendam and Van der Wiel[54] investigated the energy level structure of Ne^- by a very elegant free–free absorption experiment. In this experiment the incident electron (with the proper energy) is temporarily ($\sim 10^{-13}$ s) trapped by neon. In the second step a laser-induced transition takes place to a higher negative ion state. In subsequent steps the excited Ne^- autoionizes to produce excited neutral Ne, which in turn decays by UV photon emission. By tuning the laser wavelength and detecting the UV photon emission, one can utilize the two-state resonance enhancements and the high-resolution capability of the laser to do spectroscopy on a short-lived negative ion.

Concluding Remarks

The range of electron impact spectroscopy has been indicated here through a few simple examples. The main advantages of electron impact spectroscopy are the elimination of optical selection rules in excitation processes and the ability to scan the spectrum from the infrared to the X-ray region with the same experimental setup. More detailed information about the excitation processes can be obtained by measurements in which the scattered electron is detected in coincidence with secondary particles (electrons, photons, ions). The discussion of these topics is, however, beyond the scope of the present Account.

The experimental techniques and calibration methods for generating accurate electron impact cross sections became available only very recently, and one can expect a large body of reliable cross section data in the coming years. The application of coincidence techniques will enable us to reveal the details of complex excitation, dissociation, and ionization processes and to investigate electron and nuclear spin effects, the degree of coherence in simultaneous excitation of overlapping states, etc. The application of lasers in connection with electron impact phenomena represents a virgin area where activities are just beginning. Finally, extension of the present day techniques to excited and ionic targets, to free radical species, to complex molecules, and to solid surfaces can be expected in the near future.

I express my gratitude to my collaborators whose work is quoted in this article. This work was supported by the National Aeronautics and Space Administration through Contract NAS7-100 to the Jet Propulsion Laboratory, California Institute of Technology.

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Molecular Multiphoton Ionization Spectroscopy

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When very intense visible or ultraviolet light interacts with molecules a great many interesting things can occur which do not happen under normal illumination conditions. Multiphoton processes can occur in which several photons interact simultaneously with the molecule, in contrast to the normal situation of just a single photon being absorbed or emitted at a time. Improbable as these transitions may be, they can be used to raise a molecule into one of its excited electronic states if the photon flux is great enough. With currently available pulsed dye lasers not tuned to a direct absorption of a molecule, even though just one photon in 10^{10} gets absorbed, there are so many photons in a pulse that one can excite every molecule in a focal region. The electronically excited molecule is still bathed in a very intense field of radiation and can absorb additional photons until it is removed from a resonant condition by ionization, dissociation, reemission of photons, or the end of the light pulse. The means by which a molecule loses its excess energy, be it by ionization, emission of a photon, decomposition, or radiationless transition, can be used to detect the existence of that electronic state and thus be used as a means of knowing when a multiphoton transition has taken place. And the wavelength dependence of multiphoton transitions reveals much about the electronic structure of the molecule. For many excited electronic states their most probable fate in an intense light field is ionization, and I will discuss the use of multiphoton ionization (MPI) as a technique for the elucidation of excited-state structure,

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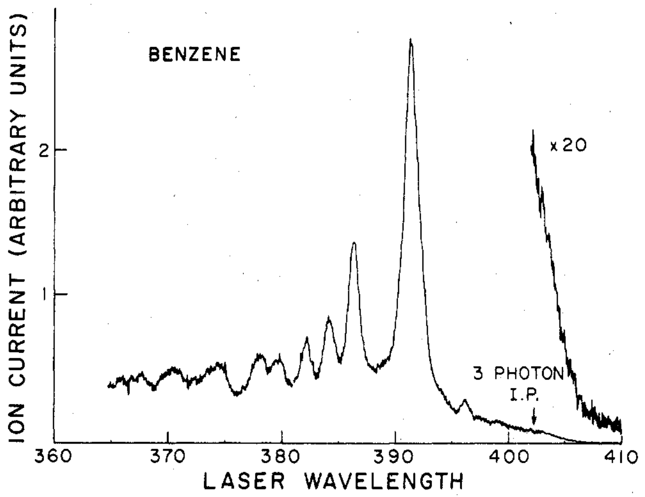

Figure 1. The multiphoton ionization spectrum of benzene which shows a newly found transition to the $^1E_{1g}$ state. A one-photon absorption would lie at half of the wavelength shown.

spectroscopy, and photochemistry. We are finding that MPI is a very simple and useful technique for recording electronic spectra of molecules, providing insight into excited states which have not been amenable to investigation by conventional spectroscopy.

The use of multiphoton spectroscopy as a tool in the investigation of excited-state spectroscopy and structure has been discussed a great deal recently, including an Account by W. M. McClain in which two photon transitions detected by absorption or fluorescence are discussed.[1] A primary advantage of using a multiphoton transition instead of a single-photon transition to determine structure is a difference in selection rules. The most striking change in using multiple photons is that a transition which involves an even number of photons in a molecule that has a center of symmetry has the selection rule g ↔ g rather than g ↔ u which must occur in transitions which incorporate an odd number of photons. Other changes occur in such rules as those concerning orbital and rotational angular momentum changes. Unfortunately, however, spin selection rules remain in effect, although spin-forbidden transitions can sometimes be overwhelmed by the vast number of photons that are available in a laser experiment.

Although no electronic transition is exactly forbidden, selection rules often cause a transition to be weak. If it is also in the vicinity of a strongly allowed transition, it will often be impossible to detect a poorly absorbing state in a normal one-photon spectrum. The use of multiphoton techniques to change the relative intensities of different electronic bands is valuable in detecting new states and in determining the symmetry and character of transitions of states whose identities are often masked by congestion and diffuseness in their transitions. For example, Figure 1 shows the spectrum of a $^1E_{1g}$ Rydberg state (one in which the excited electron is in an atomic-like orbital, in this case 3s) found in benzene[2] which had been previously hidden by the intense transition to the $^1B_{1u}$ valence state. The one-photon absorption spectrum shows no hint of a state here. When this state was discovered, we were looking for the mysterious missing $^1E_{2g}$ valence state, which is predicted by simple orbital theories. Other advantages of multiphoton techniques are that one is able to use visible photons to cause transitions to very highly excited states, avoiding experimental difficulties in the use of vacuum ultraviolet light, and one uses lasers whose spectral band width can be made narrower than that of the best of high-resolution spectrographs. The very narrow band width of the laser is useful because of the possibility of doing Doppler-free spectroscopy in a multiphoton transition. In addition, certain techniques such as polarization enable absolute state assignments[1] and, as we will see later, detection of species in supersonic nozzle beams allows the determination of structural and dynamic characteristics not possible to be determined in a nonlaser experiment.

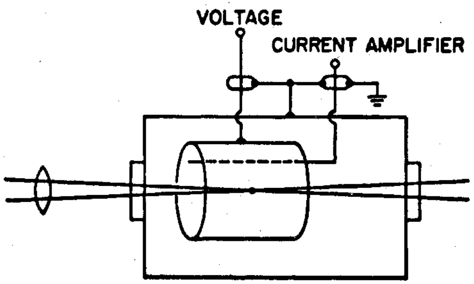

Figure 2. Schematic diagram of a cell commonly used in MPI experiments.

Technique

In order to understand what is occurring in a multiphoton ionization experiment let us examine the recording of a sample spectrum. Say we have a tunable dye laser which is capable of providing pulses with a peak power on the order of 100 kW. When this is focussed down to a small spot, the flux is on the order of gigawatts per square centimeter, about 10^{26} photons/($\mathrm{cm^2 \cdot s}$), but the pulse length is only 10^{-8} s. We focus our laser into a small cell containing a thin wire which is axially positioned in a cylinder biased with a negative potential. This potential drives the electrons to the wire where the electron current is detected by an electrometer or a boxcar integrator circuit. If enough voltage is applied between the wire and the cylinder, gas amplification or proportional counting can take place, increasing the gain and detectability of the electrons which are created by the laser pulse. A typical cell is shown schematically in Figure 2. The cell can be filled with a gas-phase sample at virtually any pressure, although the addition of a spectrally inert multiplier gas is recommended for very rarified species.

Now we will start scanning our dye laser from the red end of the spectrum. The test molecule we will use is 1,3-butadiene, whose spectrum[3] is shown in Figure 3 along with an energy level diagram. Starting at 470 nm we will scan down in the wavelength or up in the energy of the photon, which is to the left on the figure. The first peaks we see are three photon resonances in a four-photon ionization. That means it takes three simultaneously absorbed photons to populate an excited state of butadiene, called a resonance, and an additional photon is used to ionize the molecule. All of the photons have the same energy and come from the same beam. The peaks that are seen between 470 and 420 nm are all due to transitions to Rydberg states of bu-

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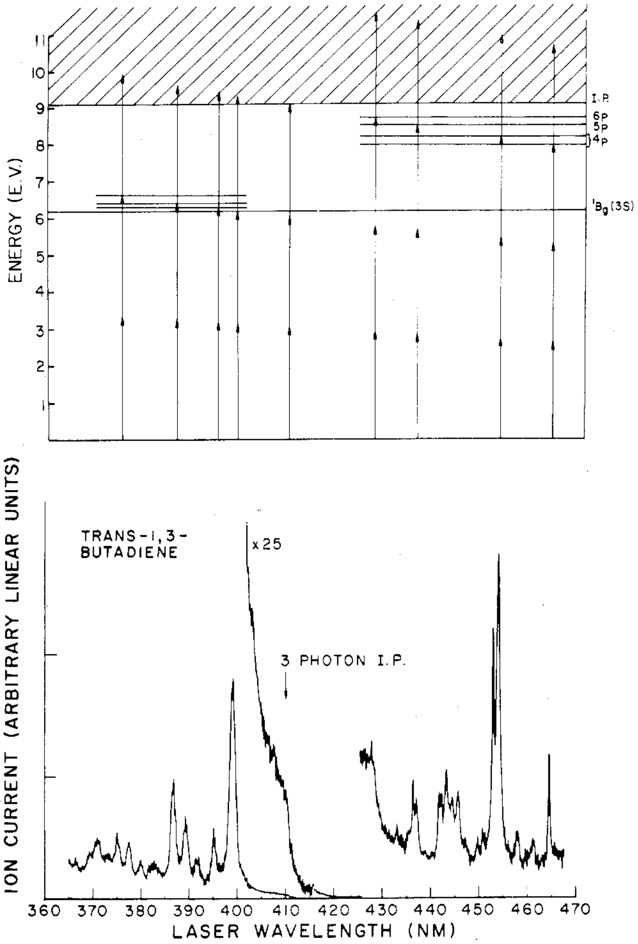

Figure 3. The MPI spectrum of *trans*-1,3-butadiene, along with an energy level diagram showing some of the states that appear in the spectrum.

tadiene, several of which are not seen in the one-photon spectrum and compose a series of states which were not known before the recording of this spectrum. As we scan up in energy of the photon, at around 413 nm we come to the three-photon ionization potential. This is the minimum energy at which ionization can take place with only three photons. We see that there is a step here and we begin to see an appreciable amount of direct ionization, where the transition to the ionization continuum is probable enough to detect ionization even without intermediate bound state resonances. With high enough light fluxes, direct ionization of a molecule can occur at any wavelength, but usually in this type of spectroscopy intensities are kept low enough that a resonance is necessary to produce appreciable signal.

Three-photon ionization is more probable than four-photon ionization and the intensity goes up until at about 400 nm we reach a new set of resonances. These are at the two-photon level and correspond to transitions to a two-photon allowed state which is seen weakly in the one-photon spectrum by virtue of vibronic interactions. In the two-photon transition this state is allowed and is detected by the subsequent one-photon ionization. In general, ionization can take any number of photons and a resonance can occur at any level. There are several ways to tell how many photons it takes to reach a resonance, but the simplest is that peaks with a given energy separation will appear closer together as more photons are required. This is because energy is being scanned twice as fast at the two-photon level, three times as fast at the three-photon level, etc. Therefore, even an approximate knowledge of expected vibrational or rotational structure will give away the energy of the state.

Although this spectrum looks fairly continuous except for the breaks in scale, it is actually a composite of several different spectra. Unfortunately a dye laser can only scan over a very limited range covered by the fluorescence width of the particular dye that is being used. Because of this, dyes must be changed every few tens of nanometers and the individual spectra are joined together to produce a spectrum such as shown in Figure 3. Even over the output wavelength range of each dye, however, a dye laser normally varies drastically in intensity. Spectral intensity comparisons would be impossible under these conditions, particularly for a nonlinear process where the exact nonlinearity is unknown (and depends upon intensity). To join various dye spectra, one must keep the output of the laser constant as the laser is scanned. We have found that the best method for this is to attenuate the pumping N_2 laser with a shutter controlled by a feedback system.[2] The spectra in Figures 1 and 3 were recorded in this manner. The others were not.

Dynamics of MPI Processes

In order to examine the dynamics of the MPI process, let us more closely consider a molecule in the process of absorbing photons. It is fair to say that most molecules are not colored, and since they therefore do not absorb visible light, it requires at least two visible photons to excite them to an excited electronic state. So for most molecules the first transition is a multiphoton process when using a visible laser. Tunable dye lasers in the ultraviolet region do not change this appreciably since they reach only very slightly into the ultraviolet. While their photon energy can be doubled using nonlinear crystals, much energy and the advantages of multiphoton selection rules are lost.

Above the first excited state in energy, the density of states is normally so high that subsequent transitions are either resonant or nearly resonant. This creates a situation in which the initial step in a multiphoton ionization is usually the rate-limiting step because it is an improbable nonlinear one, and the subsequent steps are kinetically saturated because they are single photon transitions (or nearly so) and have a much higher probability in the light fluxes being considered here. This is a great advantage in deriving information from an MPI spectrum because the structure of resonances following the initial one are not evident in the spectrum, as is seen in the example in Figure 3. For most experiments with pulsed lasers, coherent effects such as Rabi cycling are not evident in multiphoton ionization processes, so the interaction with the radiation field can be described in a simple kinetic fashion.[4-6] Equation one is a formula for the total ionization produced in a stylized square laser pulse when effects such as dissociation are taken into account. In this equation $\alpha = \sigma_I I^n$, the transition probability for the initial n photon

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event; $\beta = \sigma_{II} I^m$, the transition probability for an m photon ionization; $k_0 = 1/\tau_f$, the rate for fluorescence; k_ρ is a radiationless transition rate to a state which is not the cold ground state and does not ionize at a rate comparable to β. When the following relationships obtain,

$$A = 2 + k_0 + k_\rho + \beta$$

$$B = k_\rho + \beta$$

$$K = A/2 + \tfrac{1}{2}(A^2 - 4\alpha B)^{1/2}$$

$$L = A/2 - \tfrac{1}{2}(A^2 - 4\alpha B)^{1/2}$$

then the number of electrons produced up to time t is

$$N = \frac{\beta X_0}{(\beta + k_\rho)} \left[1 + \frac{L}{K - L} e^{-Kt} - \frac{K}{K - L} e^{-Lt} \right] \quad (1)$$

Although this equation appears somewhat formidable, it simplifies considerably when dissociation can be neglected and has some limiting forms which allow conceptualization of most processes. For example, at very low light intensities (comparatively) the signal is just proportional to the product of the cross sections for the individual steps times the intensity to the overall order of the process,

$$N = \sigma_I \sigma_{II} I^{n+m} \quad (2)$$

One usually runs out of signal before this limit is reached, however. Some order-of-magnitude values for the cross sections σ for two- and three-photon-allowed transitions are 10^{-50} cm^4·s and 10^{-82} cm^6·s^2.

I would not like to leave the impression that this simple analysis allows MPI to rest on a firm quantitative basis. A major drawback to using the above equation is obtaining a value to use for the intensity. Most experiments are done with fairly tightly focussed beams from lasers which do not have well-characterized mode structure so the intensity distribution in the focus region is not well-known. Quantitative absolute measurements await a new generation of lasers whose qualities are better defined. However, with these qualifications, we have done an extensive analysis of relative intensities in the nitric oxide MPI spectrum[7] and find that the kinetic description seems to account for the intensities of the major portion of the spectral features.

For the case of diatomic molecules such as iodine or nitric oxide it will sometimes occur that a structured three-photon resonance is at the same laser wavelength as a two-photon transition, giving rise to anomalous intensity distributions in the spectrum. This feature does not usually appear in larger molecules where the higher excited states have quasicontinuous absorption due to broadening by radiationless transitions, and can be eliminated in small molecules by using multiple laser techniques whereby one state is kept in resonance while the spectrum of the interfering state is scanned. An example is the I_2 study carried out by Williamson and Compton.[8] Even in small molecules the interferences are usually rare because rotational selection rules prohibit the occurrence of two simultaneous resonances unless these rules allow both the transition between the excited rotational levels and the transition from the ground state, an improbable event.

The kinetic scheme that is involved in multiphoton ionization also gives us a handle on the other major dissipative processes that occur in molecules, dissociation and rearrangement. When a rapid photochemical process takes place in an excited state, it can remove the molecule from resonance with the exciting light. This is obvious in the case of a dissociation, where the fragments may each have high ionization potentials, making the total fragmentation and ionization a very high order process. However, it may also occur in a simple radiationless transition from an excited state to a high vibrational level of a lower electronic state. In the collisionless gas phase, at least, the molecules will be very hot after moving from a higher electronic state to a lower one. The Franck–Condon factors of excitation from the vibrationally hot molecule to a vibrationally cold ion are very unfavorable; thus there is an effective ionization potential of the hot molecule that is above the normal ionization potential by almost the amount of the energy contained in the vibrations. This is because the most intense transitions of the hot molecules will lead to vibrational levels of the ion which are quite high above the ground ionic level. The end result is that molecules which undergo rapid radiationless transitions may not contribute strongly to the MPI spectrum, at least at moderate light intensities. The actual rates can be included in and (in theory) numerical values can be derived from the kinetic treatment of the ionization process.

This gives rise to some interesting selectivity of excited states in the multiphoton ionization spectra. When one examines a number of these spectra it is strikingly apparent that the most common strongly appearing resonances belong to Rydberg states, those in which the excited electron is undergoing a pseudohydrogenic orbit. Since the electrons in these Rydberg orbitals are nonbonding, the Rydberg states are usually longer lived than valence states, where the excited electron is in an antibonding orbital and promotes molecular decomposition or rearrangement. Because of this selective longevity toward photochemistry, the Rydberg states show up in multiphoton ionization spectra much more frequently than valence states, particularly in larger molecules. A few stable valence states such as the $^1B_{2u}$ state of benzene have been observed, and it is expected that many first excited states will be seen in MPI spectra. However for most larger molecules higher valence states are diffuse, indicating radiationless transitions of some sort, and are not expected to be seen strongly. This has its advantages and disadvantages, of course. The advantage is that one gets to study Rydberg states without any interference from the valence states, which are usually stronger in one-photon spectra. The disadvantage is the inability to study many valence states.

There is one important class of MPI spectra which does not occur with an initial multiphoton step, ionization through a triplet state. Turner et al.[9] have recorded the ionization spectrum of pyrazine using the first triplet state as the first resonance on the way to ionization. The extremely small oscillator strength of

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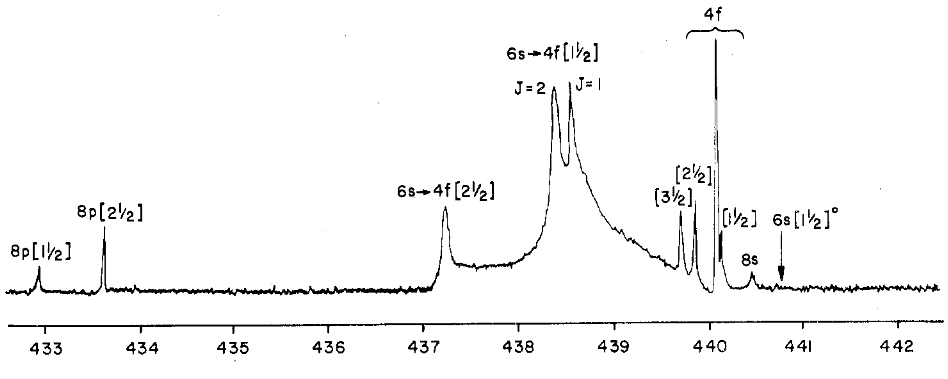

Figure 4. The MPI spectrum of xenon in the region of the expected transition to a 6s orbital. Most of this structure is pressure dependent, indicating that the transitions are taking place in a molecule-like collision complex.

the transition to the triplet is overcome by the vast number of photons that are available in the laser beam. Once a few triplet molecules are created, the ionization of these is quite rapid because no spin selection rules are violated and the multiphoton ionization proceeds in its normal manner.

Examples

On the basis of some pioneering work on the resonant two-photon ionization of the molecules C_2^- and Cs_2 by Lineberger[10] and by Collins et al.,[11,12] respectively, multiphoton ionization spectroscopy was demonstrated in 1974 to be a tool for the study of multiphoton transitions of normal molecules by our group here at Stony Brook[13] and by Petty, Tai, and Dalby.[14] Since then, many of the opportunities of the technique have been brought to light. I will present some examples which demonstrate some of its range and potential. They were obtained mostly by our group but are only representative of a rapidly growing literature.

Most of the use of MPI to date has been involved with the discovery and identification of new electronic states. Iodine[14,15] and benzene[2] were the first examples where states were seen which had been theoretically predicted but never observed because of unfavorable selection rules. Additional new states have subsequently been found in iodine,[16] ammonia,[17,18] some alkanes,[19,20] some amines,[21] polyenes,[3,22] etc.

The new state of benzene turned out to be a Rydberg state involving a 3s united atom orbital. This has been demonstrated by a transient lensing pressure broadening experiment[23] and more indirectly by analysis of the spectrum of fluorobenzene.[24] Excitations to 3s orbitals often are of a gerade type and are very weak in a transition from the totally symmetric ground state. However a two-photon transition is allowed, and MPI is an ideal way to investigate these states. Subsequent to the benzene spectrum, 3s Rydberg states were seen in several molecules by the MPI technique.[3,9,19,20,22] Knowledge of the position and structure of these states should contribute to the important question of Rydberg–valence mixing.

Even though three photons are needed to reach the higher Rydberg states of most systems and three-photon selection rules are expected to mimic one-photon rules, some new series have been found because of the change in relative intensities of the various transitions. The series seen in butadiene (as indicated previously) is an excellent example of this.

For some systems MPI can provide a means of probing excited-state repulsive potentials. One system we have studied is xenon.[25] In this case several effects make it more likely that MPI will proceed favorably during collisions in a gas at moderate pressures (>30 torr). In recording the MPI spectrum of xenon at about 50 torr one soon comes to the realization, as depicted in Figure 4, that the majority of the spectral features are due to molecular transitions. Only a few of the features are not pressure dependent, indicating a collisional enhancement. Certain of the features occur at wavelengths which correspond to energy differences between excited states of the atom, but by considering only atomic character it would not be possible to populate the lower level at the wavelengths employed. These are broad features, however, and are more representative of a diatomic molecule than of the atom. What is occurring is that the kinetic energy of a collision provides a match between an atomic resonance and the energy of the photon being used, so features are seen at energies where the energy match of the photon with the difference between the different excited atomic states is favorable but not necessarily exact. This is depicted schematically in Figure 5. The transition from the ground state takes three photons and terminates in the 6s level of an atom which is undergoing a collision. First we note that when the three photon energy is exactly resonant with the 6s atomic level, the fourth photon does not bring the atom up to the 4f level, which

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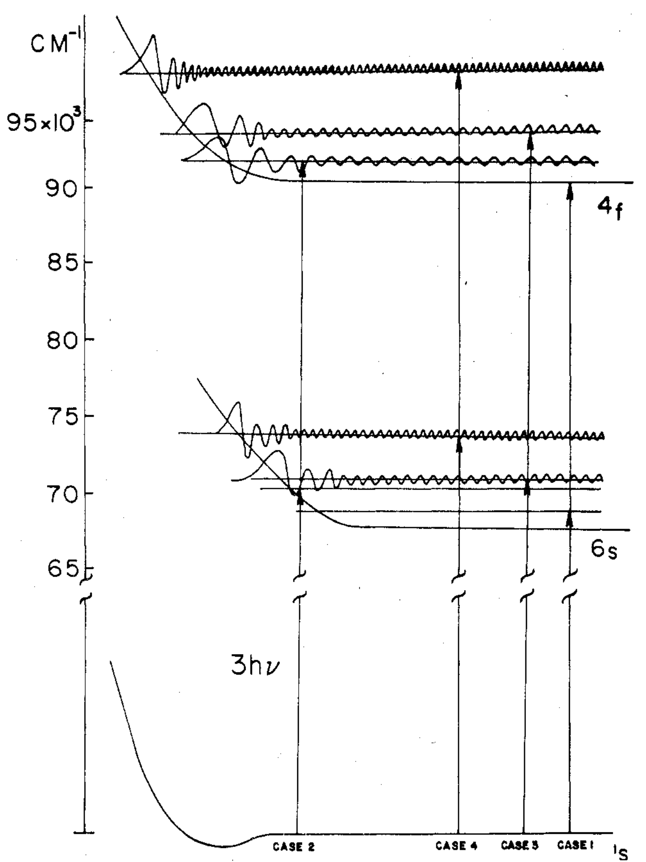

Figure 5. Potential energy curves of Xe_2 which explain the broad features seen in the xenon MPI spectrum. Transitions are taking place between continuum vibrational levels associated with excited-state repulsive curves. See the text for an explanation of the different cases.

can collisionally ionize. For this reason the 6s atomic resonance is not seen in the spectrum.

As the wavelength is scanned, the point is reached (case 1) where the 4f level(s) become resonant. Further increase of the photon energy creates a situation where the continuum vibrational function of the 6s level has the same frequency at the turning point as the lower energy 4f continuum function has further out (case 2). This match of frequency creates an overlap which produces a finite Franck–Condon factor ($\langle \phi_{6s}/\phi_{4f} \rangle$) for the transition between vibrational continua, and therefore a finite transition intensity.

Continued scanning of the laser increases the sum energy at the four-photon energy four-thirds times faster than that at the three-photon energy. As illustrated in case 3 this eventually creates the situation where the sum energies are both the same energy distance above the atomic levels, a situation in which the frequency of the continuum functions is exactly matched. Here the Franck–Condon factor is a maximum and a peak is seen in the spectrum at exactly the energy difference between the two excited atomic states even though the light is not resonant with the lower atomic level in the absence of collisions.

As the light is scanned to higher energy the vibrational continuum functions become such that they never have the same frequency at any internuclear distance and the Franck–Condon factor goes to zero (case 4). Transitions where the lower potential is longer ranged than the upper are thus shaded to the red, while the opposite would be the case for a transition where the lower excited repulsive curve is shorter ranged. For atoms simpler than xenon it should be possible to derive detailed information about the excited-state repulsive curves from the shape of the resonances.

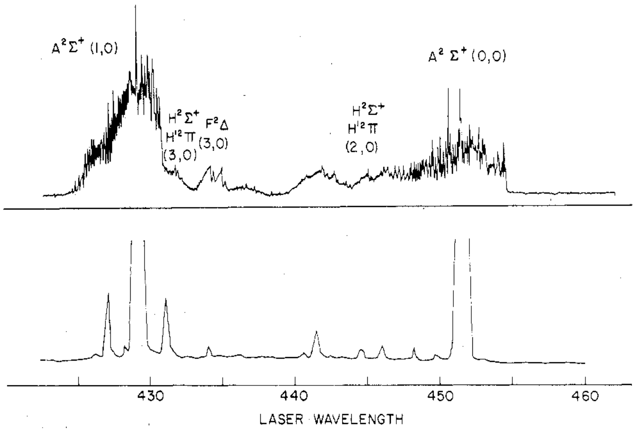

Figure 6. A comparison between the room-temperature and the low-temperature supersonic expansion MPI spectrum of nitric oxide, showing the great simplification and decongestion of the spectrum. The widths of the lines in the low-temperature spectrum (lower) are determined by the scan conditions, not by inherent width (see Figure 7).

The sensitivity of the MPI technique enables one to use more sophisticated sample containment and electron detection schemes than the one previously outlined. In fact with the laser powers available today it is possible to ionize every molecule in the focal region of the laser on resonance, although this has disadvantages in that it smears out the spectral features and care is usually taken to prevent this "saturation". However it means that just a few molecules in the focal region will give you a reasonable signal. Thus MPI can successfully provide spectra of very dilute gases or even gases seeded into a supersonic nozzle beam.[7] This latter technique can be put to great advantage because the beam propagates through a vacuum and allows the use of an electron multiplier to collect the electrons instead of a current measuring device, providing greater sensitivity. The molecules contained in a supersonic nozzle, as demonstrated by Smalley, Levy, and Wharton,[26] are cooled to rotational temperatures of the order of 1 K if contained in a helium carrier gas. Thus we are able to measure the ionization spectrum of very cold molecules, simplifying the rotational and vibrational structure of the molecules enormously. By using high-resolution lasers we are able to see the rotational structure of larger molecules in a detail that has never before been possible due to congestion and Doppler broadening. Of course in the beam the Doppler width is drastically reduced because of the fact that the molecules are all going the same direction with the same speed. Figure 6 shows a comparison between the room-temperature MPI spectrum and a low-temperature spectrum of nitric oxide contained in a supersonic nozzle beam. At room temperature the extensive rotational structure of the two-photon $A^2\Sigma$ resonances (which are off-scale in the beam spectrum) overlap and obscure the many three-photon resonances seen in this energy region. At low temperature each vibronic band is separated out and appears as a single line at this resolution. The simplification upon going to low temperatures is drastic

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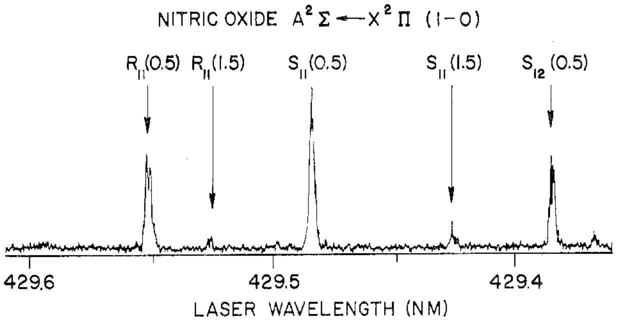

Figure 7. The rotationally resolved $A^2\Sigma \leftarrow X^2\pi$ (1–0) band of nitric oxide cooled in a pulsed supersonic expansion. This is the entire remaining structure, showing that 90% of the molecules are in the lowest rotational level in the ground state. The rotational temperature of these molecules is less than 2 K.

and greatly aids the analysis of any molecular spectrum. Figure 7 shows the entire rotational structure left in the spectrum of a single vibronic band of nitric oxide seeded in helium. The rotational temperature of the sample in this spectrum is less than 2 K. In addition to the improved resolution and the possibility of extracting rotational constants from the spectrum, it is also possible to extract natural line widths from the rotational lines because the Doppler effect is limited and thus to determine the lifetime of each rovibronic level.

MPI has shown its usefulness in providing the type of new spectral data illustrated above, but the dynamics of the multiphoton excitation are best studied in a molecule with very well-characterized excited states. One of the best examples of this is nitric oxide, which could be called the sodium atom of the molecular world. The unpaired electron in an antibonding orbital is as loosely bound as the outer sodium electron and forms excited states in a very atomic-like way.

The room temperature spectrum of nitric oxide is too complicated to interpret, but at the low temperatures of a nozzle experiment individual vibronic lines separate out nicely as in Figure 6 and intensity comparisons can be made. We analyzed this four-photon ionization region of the spectrum in which there are both two-photon and three-photon resonances.[7] The two-photon resonances are found to be much more intense than the three-photon ones, in agreement with the kinetic treatment outlined previously. Calculation of the transition intensities via a perturbation theory approach is found to reproduce the relative intensities of the different transitions fairly well.[4] However, some anomalies point out the necessity of including dissociation in the kinetic scheme as well as considering the ionization cross section for some excited states where the transition probability to the continuum is small.

The fact that usually all of the spectroscopy in an MPI experiment originates from the initial multiphoton step allows one to examine the polarization characteristics of this transition. In any nonresonant multiphoton transition, second and subsequent photons can be thought of as acting on molecules "photoselected" by the first photon. The sample of molecules excited will depend upon the relative directions and magnitudes of the molecular transition moments to the polarization vector of the light and thus will depend upon the symmetries of the states involved in the transition.[1] Thus the use of circularly polarized light vs. linearly polarized light, for example, will result in a different signal intensity. The ratio of the signals created by the two types of light is a valuable indication of the symmetry of an excited state. When using a single laser, the ratio of circular to linear is 3/2 for all non-totally-symmetric two-photon transitions and for all non-Q branches no matter what the symmetry of a transition. For Q branches of symmetry-preserving transitions, however, the ratio can range from 0 to 3/2. This effect was exploited by Dalby et al. in their original work on iodine[15] and has been more recently exploited by Berg, Parker, and El Sayed[27-29] and by Nieman and Colson[18] to establish some state symmetries.

Another interesting application of MPI is the determination of ionization potentials, which can be determined from the rapid onset of an n-photon ionization potential.[30,31]

Concluding Remarks

It appears that there is a whole new direction beginning for MPI spectroscopy—that involved with mass analyzing the ions that are produced in the experiment.[32-35] It is found that extensive fragmentation can take place with higher laser powers, leading to ions which energetically require the absorption of as many as nine photons. The mechanism of the fragmentation is of great interest and is a current active field of research.

The use of MPI as a spectroscopic tool is growing quickly, with new refinements being introduced at a rapid rate. The next few years are likely to see the combination of MPI with photoelectron spectroscopy, many ultra-high-resolution spectra, and multiple laser experiments to sort out complicated multiple resonances and probe photochemical pathways. The extreme sensitivity of MPI for many molecules suggests analytical uses, which are being pursued by several groups. Improvement in laser technology will continue to open up new classes of molecules for study as higher resolution and higher energy photons become available in ever larger quantities. As photon intensities and energies go up, multiphoton ionization is bound to be one of the aspects to be considered in any laser experiment, and our understanding of this phenomenon will provide many returns not only in the understanding of molecular structure and behavior but also in the design of any experiment using high-intensity light sources.

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