The multiphoton ionization spectrum of xenon: Interatomic effects in multiphoton transitions

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The multiphoton ionization spectrum of xenon was taken in the vicinity of the laser wavelengths corresponding to one-third the energy of transitions to the $5p^{5}(^{2}P_{3/2})6s$, $5p^{5}(^{2}P_{1/2})6s$, and $5p^{5}(^{2}P_{3/2})5d$ atomic levels. Many atomic resonances were observed, the most prominent being third photon resonances with atomic 5d levels and fourth photon resonances with atomic 4f levels. However, peaks corresponding to ionization through the 6s levels were weak or absent. Resonances in these regions showed extreme pressure dependence. At higher pressures (> 50 torr) a broadening of the atomic lines as well as the existence of continuum backgrounds and strong broad resonances peaking at the energy of transitions between excited states were seen. At low pressure (40 torr) the atomic lines were interpreted to be a consequency of resonances with vibrational continua of excited state diatomic xenon molecules and illustrate the necessity of inclusion of molecular Franck-Condon factors into the multiphoton ionization probability of atomic gases at moderate pressures.

Multiphoton ionization (MPI) spectroscopy probes the excited state structure of atoms and molecules in such a way that the information obtained is complementary to conventional one photon spectroscopy. However, only a few systems have been studied to date, and even the qualitative aspects of MPI spectra cannot yet be anticipated, much less calculated. The most frequently studied systems have been the alkali metals, both as atoms and diatomic molecules.¹ These species have very low-lying excited states and low ionization potentials so that ionization occurs with only two or three photons. In general, in the ionization of these systems each photon has been resonant with some excited state, although sometimes it is a vibrational continuum which provides an energy match. Iodine is another diatomic molecule which has been studied.² In that spectrum the first photon is resonant only with a dissociation continuum and an interesting bound resonance occurs after the absorption of the second photon of a three photon ionization.

A slightly different class of MPI spectra occurs when the atom or molecule has no low-lying excited states. The first resonances then require the energy of two or three photons, with intermediate virtual states being completely nonresonant (except with highly excited vibrational levels of the ground state for which Franck-Condon factors are exceedingly small). The detailed nature of these virtual states cannot, therefore, be described as being predominantly similar to any given excited state and the transitions in these spectra are more similar to those of multiphoton spectroscopy than to those of conventional spectroscopy. Atomic systems such as the alkaline earth metals³ have been studied. Molecular spectra of this type have been recorded for nitric oxide,⁴ benzene,⁵ butadiene,⁶ and hexatriene.⁷

Extreme examples of multiphoton ionizations with nonresonant intermediate states have been reported for the rare gas atoms. Helium has been ionized with as many as 22 photons from a neodymium laser.⁸ Even for xenon it takes three or four dye laser photons to reach the lowest excited states, while four or five photons are needed to ionize this atom. It is of interest to see what effects these many photon transitions have on the MPI spectrum of an atom.

In the work reported here it is found that the effects are fairly extensive. In contrast to previous work on metal vapor systems it is quite easy to vary the pressure of a stable gas. This has enabled us to separate collisional effects from those of the isolated atoms and it is found that the majority of features in the MPI spectrum at moderate pressures are in fact due to collisionally promoted transitions. It is clear from these spectra that vibrational continuum functions play a large role in providing a mechanism for energy resonance and that collisions play a prominent role in allowing otherwise forbidden states to be used in constructing virtual levels. It is important that the extreme pressure dependent effects seen in the spectrum of xenon be considered in the interpretation of all MPI spectra.

EXPERIMENTAL

The multiphoton experimental apparatus has been described in previous publications. ^{5,6} A 1 MW nitrogen laser pumped a Molectron DL 200 dye laser of maximum output of 120 kW. The bandwidth of the laser output was 0.02 nm and the repetition frequency was 10 sec⁻¹. Dye laser output was measured with a Molectron J305 pyroelectric joulemeter. The dye laser was scanned with a stepper motor drive and calibrated by comparison to known mercury lines through a monochromator of absolute accuracy of 1 Å. Maximum dye laser output was needed for all of these experiments, which prevented taking spectra at constant intensity as has been done previously. ^{5,6}

The light from the dye laser was focused into a metal gas cell by a 12 mm focal length diffraction limited lens (Special Optics). The gas cell contained a cylindrical electrode around a 0.020 in. wire electrode. Both were stainless steel. The signal from the gas cell, which was normally biased (depending on the experiment) from 50 to 325 V with the cylinder negative, was passed through a current amplifier and into a dual channel PAR boxcar averager operated in a baseline subtraction mode, and from there to the chart recorder.

It must be noted that at the higher applied voltages strong gaseous electron multiplication occurs at low pressures. This multiplication was significant above approximately 50 V and for this reason at high voltages peaks in the low pressure spectra often exhibited enhanced intensity relative to spectra taken at higher pressures. If the signal-to-noise ratio permitted, therefore, spectra were run at the lower applied bias voltage.

All spectra were taken at pressures ranging from 1 to 100 torr. Pressure inside the sample cell was monitored with a Datametrics barocel electronic manometer connected to the cell. Once the cell was filled with xenon the pressure was varied by freezing the xenon into a section of stainless steel tubing attached to the cell and then by allowing the desired xenon pressure to reenter the cell.

The xenon used in this work was Research grade from Matheson and was used without further purification.

RESULTS

Atomic xenon exists in the ground state as $\dots 5s^25p^{6}$ ¹S. The Xe I ion exists as $\dots 5s^25p^{5}{}^2P_{3/2}$ and ${}^2P_{1/2}$ as its lower and upper states, respectively. The 2P interval is 10 537 cm⁻¹ which shows the magnitude of the spin-orbit interaction. A diagram of the atomic levels pertaining to these experiments is shown in Fig. 1. It must be remembered that xenon follows the (j,j) coupling scheme and thus the selection rules for electric dipole radiation are $\Delta J = 0, \pm 1$ and $0 \leftrightarrow 0$ for each single photon step.

Three regions of the spectrum were investigated: the first (430-442 nm) using coumarin 120 dye, the second

TABLE I. Peak assignments for MPI spectrum of xenon.

Laser λ (nm)	v Vacuum laser (sec⁻¹)	x-photon resonance	\tilde{v} Vacuum for x-photon resonance	Line designation
440.50	22 701.3	4	90 805.0	$8s[1\ 1/2]\ J=2$
440.29	22712.5	4	90850.0	$4f [1 \ 1/2] \ J = 2$
440.23	22715.5	4	90 862.0	$4f[4\ 1/2]J=4$
439.99	22727.7	4	90910.6	$4f [2 \ 1/2] J = 2$
439.83	22736.2	4	90944.7	$4f[3 \ 1/2] J = 4$
438.70	22794.6	•••	•••	$4f [1 \ 1/2] J = 1 - 6s$
438.51	22 804.3			$4f [1 \ 1/2] J = 2 - 6s$
437.35	22 864.9			$4f[2\ 1/2] - 6s$
433.73	23 056.2	4	92221.9	$8p[2 \ 1/2] \ J=2$
433.03	23 092.9	4	92371.4	$8p[1 \ 1/2] \ J=2$
432.03	23 140.1	4	92560.5	$8p[0\ 1/2]\ J=0$
388.40	25 747	3	77240	[molecule]
384.88	25 982	4	103 928	5f' [autoionized]
384.02	26040.1	3	78120.3	$6p[2 \ 1/2] J = 2$
383.46	26 078	3	78235	[molecule]
382.5	26144	3	78431	[molecule]
370.4	26990.6	3	80 970, 9	$5d[3 \ 1/2] J=3$
363.8	27 477.06	3	82430.7	$5d[2 \ 1/2] J=3$
363.3	27529.3	a	а	a
362.9	27 548.2	a	a	a
362.5	27598.3	a	a	a
361.1	27685.2	a	а	a

^aUnassigned in this work.



FIG. 1. Energy level scheme for pertinent atomic levels of xenon, as taken from Ref. 9. Primed levels indicate those levels belonging to the higher ion limit. Arrows represent a five-photon ionization process with a fourth-photon resonance with an atomic 4f level. From Mulliken's work (Ref. 14) it is clear that each atomic level is an asymptote for a manifold of case c molecular potential curves resulting from xenon molecules dissociating to a ground state atom and an excited state atom.

(381-391 nm) using BBQ dye (4, 4''' - bis-butyloctyloxy-quaterphenyl), and the third region (359-371 nm) using BPBD dye [butyl-2-phenyl-5(4-biphenyl)1, 3, 4-oxadia-zole]. Each of the regions shows very broad as well as narrow peaks and the spectra exhibit a marked pressure dependence.

The 430-442 nm region encompasses the wavelength at one-third the photon energy of the 146.9 nm atomic excitation $5p^{5}(^{2}P_{3/2})6s - {}^{1}S_{0}$. Ionization here would occur in the fifth photon. No peak was seen in any of the spectra at 440.8 nm corresponding to resonance in the third photon with the $5p^{5}(^{2}P_{3/2})6s$, J=1 atomic level, though for three photons this $\Delta J = 1$ transition is allowed. The spectra of this region at various pressures are shown in Fig. 2. In addition to the peaks in the figure several more lines were seen in the 431-434 nm vicinity corresponding to resonances with 8p atomic levels (see Table I). At higher pressures the spectra were dominated by two broad peaks with a long continuumlike tail to the red. These broad peaks were absent in the low pressure spectra where a narrower line at 440.23 nm showed increasing intensity (Fig. 1).

By comparison with Moore⁹ the lines were given assignments as indicated in Table I, using standard Racah notation. Thus, the spectrum contains peaks which correspond to a resonance in the fourth photon with purely atomic energy levels, as well as peaks corresponding to excitations from an excited $5p^{5}[^{2}P_{3/2}]$ 6s level to 4f levels. However, there is no peak corresponding to the $5p^6 \rightarrow 6s$ excitation itself, indicating that that level is being populated off resonance in a process involving diatomic xenon molecules, i.e., the photons are in resonance with both a molecular level dissociating to a 6s atom and also with the energy difference between that 6s molecular level and a 4f molecular level. This molecular aspect is confirmed by the pressure dependence of the spectra. At the high pressures where the likelihood of two xenon atoms approaching one another into the Van der Waals well is increased the broad "molecular" peaks are much stronger than the narrow, atomic peak. At low pressure the intensity relationship is reversed, with the atomic peak appearing strong and the molecular peak absent.



FIG. 2. Spectrum using coumarin-120 dye at xenon pressures of 90, 20, and 10 torr and an applied bias voltage of 50 V. The large peaks at higher pressure are due to 4f + 6s molecular transitions, i.e., the photons are in resonance with both a molecular level dissociating to a 6s atom and also with the energy difference between that 6s molecular level and a 4f molecular level. The lines near 440 nm represent fourth photon resonances with atomic 4f levels. Complete peak assignments are given in Table I.



FIG. 3. Spectrum of xenon at 50 torr taken with BBQ dye and an applied voltage of 325 V. Narrow lines are assigned resonances with atomic levels indicated. Broad lines are due to molecular resonances (see text). See Table I for complete peak assignments.

The second region investigated is in the vicinity of one-third the photon energy for the $5p^{5}({}^{2}P_{1/2})6s - {}^{1}S_{0}$ excitation. This is an atomic level converging to the higher ion limit of xenon. Again, at the higher pressures no peak was seen at the photon energy corresponding to the three-photon excitation to the $5p^{5}(^{2}P_{1/2})6s$ atomic level, but as before there were both broad and narrow peaks with a large background continuum (Fig. 3). The continuous spectrum probably extends to still higher energy but is not seen because of declining laser intensity. As the pressure was lowered in these scans only the broad peak at ~ 383.3 nm remained. At pressures below 5 torr that peak was very narrow and, in fact, was shifted to 388.8 nm, the position of the atomic line (Fig. 4). Thus, the higher energy broad peaks as well as the continuum are assigned as resonances in the third photon with molecular levels dissociating to a $5p^{5(^{2}P_{1/2})}6p$ atom and a ground state atom (see Table I). It is clear that there is a manifold of energies in the 6pstates to which excitation could occur. Examination of the sharp lines shows the line at 384.80 nm as having a typical Fano line shape for autoionized lines¹⁰ and accordingly has been assigned as a fourth photon resonance with a 5f' autoionized level.¹¹ The sharp line at 384.02 nm could be assigned to a three-photon resonance with the $5p^{5}({}^{2}P_{3/2})6p[2 1/2] J = 2$ level.⁹ With three photons this is a forbidden level for an electric dipole transition. It is allowed, though, in electric quadrupole or magnetic dipole transitions and has been seen as an electric quadrupole-allowed excitation with one photon.¹² The prominent peak at ~ 388.3 nm is assigned as resulting from excitations involving collisions of $5p^{5}(^{2}P_{1/2})6s$ at-



FIG. 4. Spectrum showing shift of the 388.8 nm $5p^{5}(^{2}P_{1/2})$ 6s + ¹S line with pressure: (a) 50 torr and (b) 1 torr, and an applied voltage of 75 V.



FIG. 5. Spectrum using B-PBD dye. Dye intensity rapidly drops to the blue of 363 nm. The prominent peaks were assigned as third photon resonances with atomic 5d levels. See Table I for complete peak assignments.

oms and ground state atoms at higher pressures, and as the unperturbed atomic excitation at low pressures.

The highest energy region investigated was the region corresponding to the three-photon excitation of various $5p^{5}({}^{2}P_{3/2})5d$ levels. Strong signals were seen at energies corresponding to three photon $5p^{5}[{}^{2}P_{3/2}]5d[2\ 1/2]J$ $= 3 - {}^{1}S$ and $5d[3\ 1/2]J = 3 - {}^{1}S$ excitations (Fig. 5). These peaks became broadened as the pressure was increased to 100 torr; this too was interpreted as resonance with molecular states derived from the corresponding 5d atomic states. In addition, several more lines of irregular spacing were seen in the extreme blue end of the spectrum (Table I). They were not assigned in this work.

DISCUSSION

The features of these spectra can be explained by examination of the proposed potential curves for ground state and excited state xenon diatoms. Freeman et al. 13 have determined the ground state potential curve of the diatomic xenon molecule. It is a repulsive state with a Van der Waal's well of 0.024 eV at 4.4 Å. It is well known that the rare gases form strongly bound diatomic molecules in their excited states. Mulliken¹⁴ has proposed a set of potential curves for some of the lower excited states of Xe2, and he noted the existence of major humps in certain curves in addition to the strictly repulsive and attractive potentials. From his curves it is clear that a manifold of case c stubstates joins onto each atomic asymptote. In addition, from calculations on excited states of He2¹⁵ and Ne2¹⁶ Mulliken's curves can be modified to bring out several points. First, the Van der Waal's well of the ground state molecule occurs at a much larger nuclear separation than the excited state wells. Secondly, these excited state wells in turn occur much closer in on the potential curves than the aforementioned humps, at a nuclear separation where the ground state potential is steeply repulsive. Thirdly, and most importantly to these spectra, the excited state potentials are already repulsive at larger nuclear separations where the ground state potential curve is still flat. The resultant picture then predicts repulsive sections of the excited state curves corresponding to nuclear separations comparable to the R_e of the Van der Waal's ground state well.

Consequently, a multiphoton ionization of a xenon quasimolecule might employ vibrational continuum states of the repulsive portions of the molecular excited state curves as intermediate resonances. This can be seen by considering the standard repulsive eigenfunctions¹⁷ of the repulsive sections of the proposed potential curves for rare gas diatomic molecules.^{15,16} We will discuss the resonances in a perturbation theory picture where virtual states and intermediate resonances are constructed by a sum of all the stationary atomic states, interacting with neighboring ground state xenon atoms where necessary. The standard multiphoton transition sums¹⁸ will then contain electronic matrix elements which are dependent upon an internuclear distance R, e.g., $\langle \Psi_1(R) | z | \Psi_2(R) \rangle$, each of which are multiplied by Frank-Condon factors between continuum vibrational wavefunctions. These latter have a pressure dependence by virtue of the increase in the magnitude of the continuum wavefunction at a given R as the probability of finding that R in the ensemble increases. Each of the sums in the perturbation expression¹⁹ defines a virtual state, which can degenerate to a single dominant term at a resonance.

This study of xenon is remarkable in that the majority of the features and intensity contained in our spectra are characteristic of these molecular levels rather than the atomic energy levels one would associate with a monatomic gas. Certain features, those which have atomiclike line shapes, have been called "hybrid" resonances by Collins et al. when they appeared in the MPI spectrum of cesium¹ and rubidium.²⁰ In those systems resonances appear at the energy of transitions between excited states in the same way as the 4f - 6s resonances appear in xenon. Collins et al. account for the energy mismatch by invoking a picture whereby the atoms move out on a repulsive potential curve after the absorption of the first photon, but before the second photon is absorbed. Each photon is resonant with some excited state potential curve in those atoms with low energy excited states. This picture is consistent and plausible for the alkali case where one-photon transitions are involved exclusively and the experiment employes a fairly low power dye laser. In that case sequential absorptions may actually occur.

For the case of xenon, where the final resonance is at least three photon energies above the ground state and the laser powers are 10 to 100 times those used in the alkali experiments, the sequential photon absorption picture is not reasonable. From simple kinetic arguments it is clear that if there is enough light to cause a three-photon transition subsequent single-photon transitions should certainly take place before the internuclear distance changes in a classical sense. Another way of saying this is that at the powers necessary for this type of experiment any single-photon resonances are partially saturated, shortening the lifetime of the excited state and forcing a simultaneous absorption picture.²¹

In order to fully explain all of the resonances of xenon

it would be necessary to develop a theoretical model which can account for relative intensities. These in part depend upon such dissipative processes as emission and collisional ionization which take place on a time scale longer than the excitation. Also, the theory must include the proper discrete and continuous vibrational functions which are important in a simultaneous excitation. A comprehensive approach which includes channels in which coherence is lost has not been developed so we can only discuss the spectra in a qualitative way.

All but three of the lines seen in our spectra decrease in intensity when the pressure is decreased. These exceptions are the $4f[4 \ 1/2]J = 4$ line and the two 5d lines $[3 \ 1/2]^0 J = 3$ and $[2 \ 1/2]^0 J = 3$. Some of the pressure dependent atomic lines become diffuse at higher pressure while others stay narrow and atomiclike, as in the hybrid resonances of Collins et al. The narrow pressure dependent lines, all of which are four-photon resonances in these spectra, seem to be made allowed by long-range interactions. The pressure dependence of a narrow atomiclike resonance may be explained by the occurrence of a small symmetry breaking interaction. This would help to increase the transition probability by allowing states to be included into the virtual level sums which would otherwise not contribute to the intensity for symmetry reasons. Thus, for example, the 4f resonances could use the 6s levels in the second as well as the third virtual state sums. For reasons outlined below the 6s curve has a longer range interaction than the 4f curves and a virtual state perturbation could occur without a significant change in energy of the 4f level.

The five photon ionization through the 5f' autoionizing level is another transition which relies upon collisional perturbations providing a resonant virtual state. The third-photon energy lies in the region of the 6p levels, which are parity forbidden for three-photon transitions. As seen in Fig. 3 at higher pressures these states form a continuum which is an intermediate resonance for the 5f' state. The autoionizing state does not seem to be significantly broadened beyond a normal Fano line shape although it is not possible to say whether the autoionization is collisionally enhanced since the absorption line shape is not known at low pressures, the position being previously known from emission spectra.¹¹

Near the 5f' line is a peak which corresponds to the $6p[2\ 1/2]J=2$ excitation in three photons. Although this is parity forbidden for both one- and three-photon transitions, it also appears in one-photon absorptions at high pressures.¹² If the parity were disturbed by a strong collision, one would expect this line to blend into the continuous background. Either the transition is made allowed by a quadrupole step in the excitation or else very long-range collisions, which do not significantly change the energy, are sufficient to break the symmetry enough to allow the transition to occur. The latter explanation is more likely, although it is not clear why this transition differs from the others involving 6p orbitals.

To higher energy of the 6p continuum the transitions to 5d orbitals are the first truly allowed three-photon resonances in a four-photon ionization. They are very strong transitions. To the blue of the $5d[2 \ 1/2]^0 J = 3$ line at 363.8 nm the series of sharp absorptions is somewhat mysterious. The spacings are of low frequency but they cannot be due to transitions from the ground state Van der Waal's well since that shallow potential could not support the whole irregular series. Vibrational levels of one or more excited potentials could give any pattern, but it would be quite coincidental that the lines would fall immediately adjacent to an allowed line. The structure cannot be caused by resonances in the four-photon continuum because the four photon energy is above the ${}^{2}P_{1/2}^{0}$ ionization limit where there is no autoionization structure. Unfortunately, these lines are on the extreme high energy limit of the dye laser and structure seems to extend past this limit. Continuation of studies to higher energy should produce some interesting information about the excited state potentials of Xe₂.

Since the 6s resonance lines are so strong in one-photon absorption spectra and since three-photon transitions include the same selection rules as one-photon transitions, one would expect to see these lines prominently in the MPI spectra. In fact, we have never seen the $6s[1 \ 1/2]^0 J = 1$ line, and the $6s'[0 \ 1/2]^0 J = 1$ transition is recognizable as an atomic line only at low pressure and is quite weak. The reason for the weakness of these resonances is that they both would require the energy of five photons to ionize the atom in the lowest order approximation. Apparently, the transition probability for the five-photon ionization through the $6s[1 \ 1/2]$ J = 1 resonance has a much lower probability than ionization through 4f resonances (which are prominent lines neighboring the 6s wavelength) via collisional ionization. That is to say a three-photon step followed by a two-photon step is less probable than a four-photon step followed by collisional ionization. The lack of a 6s resonance may be an indication that the excitation maintains coherence, making the former a higher order process than the latter.

The 6s' resonance line is seen clearly although weakly at low pressures but broadens greatly and shifts when the pressure is increased (Fig. 4). Four photons of the energy needed to make the 6s' state resonant with three photons is above the ${}^{2}P_{11/2}$ ionization limit but below the ${}^{2}P_{1/2}$ limit. Since the core after the 6s' excitation is ${}^{2}P_{1/2}$, ionization after four photons would be an autoionization, accounting for the weakness of the transition. Either the autoionization, or the virtual state transitions, or both are enhanced by collisions and the intensity increases with pressure while the line shifts to higher energy until it blends into the continuum apparently due to the 6p transitions.

Although the $6s[1 \ 1/2]J = 1$ level does not appear as an atomic line in the MPI spectrum, some of the most intense lines in the spectrum are due to it. The broad features at 437-439 nm have their peaks at precisely the energy of the allowed 6s - 4f transitions. They can be qualitatively explained by considering the 6s and 4f potentials and continuum vibrational functions of Xe₂. It is well known that for rare gas diatomics molecules many potential curves are repulsive at large distances

due to the unfavorable overlap of the Rydberg electron of the excited atom with the filled core orbitals of the unexcited atom.¹⁴ This repulsive energy goes as the square of the overlap for Σ states and varies in magnitude and range depending upon the principle quantum number and angular momentum of the Rydberg orbital. The larger the principle quantum number the more extended is the orbital, and hence the repulsion is longer range, leading to the expectation that the 6s curves of Xe₂ would rise before the 4f curves. With this information the appearance of the broad features becomes clear. Since a three-photon resonance in a four-photon excitation to any 4f level always lies above the 6s asymptote, no exact resonance with both levels can occur in the isolated atom. However, if one considers the diatomic molecule, then resonance is exact due to the vibrational continuum, but the transition probability is tempered by a Franck-Condon factor between two vibrational continuum functions. For a limited range the wavelength of these continuum functions is dependent upon the distance from the classical turning point. The line shape is determined by the Franck-Condon factors for the two states with different R dependences. Denoting the energy mismatches with the atomic states in the third and fourth steps as ΔE_3 and ΔE_4 , respectively, as one scans up in laser energy (E_1) , when the 4fresonance is first reached ($\Delta E_4 = 0$) the kinetic energy involved in the 6s resonance (ΔE_3) is already finite so the frequencies of the continuum functions do not match, making for a weak transition. As the laser energy is scanned higher the energy swept at the four-photon level $d\Delta E_4/dE_1$ is 4/3 that swept at the three-photon level $d\Delta E_3/dE_1$ so the wavelengths of the continuum functions gradually come to be the same and in phase over an ever larger range of R values. If the lower excited potential is longer range, then the increase of the wavelength of the 6s continuum function at the turning point allows a nonzero Franck-Condon factor as long as ΔE_3 $\geq \Delta E_4$. This is because the longer wavelength of the lower function near the turning point can favorably overlap the upper function, which at that point has gained most of its asymptotic frequency. When $\Delta E_3 = \Delta E_4$ there is a peak in the overlap of the continuum functions and therefore a peak in the ionization probability. This is, of course, just the energy of a 6s - 4f transition in the isolated system. When $\Delta E_3 < \Delta E_4$ there is no matching of the wavelengths of the continuum functions at any nuclear separation, so the absorption drops off sharply to high energy of the peak. At pressures greater than a few torr the advantage of having two resonances in the excitation more than offsets the necessity for including internuclear considerations. At the same time the atoms retain much of their individuality, since the lines that are seen are exactly the ones expected from consideration of only the atomic functions.

The above model qualitatively explains the broad features of the MPI spectrum. It is expected that a quantitative treatment of the line shapes could provide information about the excited state repulsive potentials which cannot be easily obtained by other methods. Since the sampling point of the excited state energy is precisely defined by the laser frequency, the inclusion of a third state into standard linewidth theory should not be difficult.

CONCLUSIONS

This study of xenon has enabled us to qualitatively understand some of the collisional effects that can occur in MPI spectra. At moderate pressures most of the features seen are not due to expected transitions in isolated atoms. The pressure dependence of seemingly atomic lines demonstrates that a quantitative theory must include the radial dependence of matrix elements included in the virtual state transitions as well as the vibrational continua of the repulsive excited state potentials. Since the spectral characteristics are due to many excited state potentials of the system, a quantitative study should be able to provide much information about interatomic interactions which is not available from other sources. In addition to the Xe₂ system the fitting of corrected MPI spectra should give information about the interaction of xenon with other rare gases, atoms, and molecules.

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