

(12,3) state and the ($\epsilon_S, 0$) Stark-induced continuum leads to autoionization of the (12,3) level into the Stark-induced continuum. Thus when the electric field depresses the lowest ionization limit below the (12,3) state, the manifestation of the interseries interactions changes from series perturbations to autoionization. This phenomenon was first observed in Ba by Garton, Parkinson, and Reeves⁴ who labeled it "forced autoionization." It was later characterized in a quantitative manner by Sandner, Safinya, and Gallagher.⁵ It is particularly important to note that the value of the field required to ionize a molecule does not depend on the principal quantum number of the (12,3) state but only on its binding energy relative to the lowest ionization limit. This makes an enormous difference in the requisite ionizing field. An $n=12$ atomic state requires a field of 17 kV/cm for field ionization,⁷ but as we shall see, the Li_2 (12,3) state can be ionized by a field of 161 V/cm.

Two Nd:YAG-pumped pulsed dye lasers (YAG is yttrium aluminum garnet) are used to excite a supersonic lithium beam first to the $v'=3$ or 4 vibrational levels of the B state, and then to the $v^*=2$ or 3 Rydberg series. The lithium beam is generated by heating a 3.2-cm-diam, 10-cm-long stainless-steel cylindrical oven, fitted with a removable nozzle having a 0.6-mm orifice. The oven is surrounded by an electrically isolated 12- μm -thick molybdenum-foil heating element which carries a typical current of ~ 150 A. The nozzle is heated separately with a coaxial Nichrome heater. The two approximately collinear laser beams cross the molecular beam at a right angle 10 cm downstream from the lithium oven nozzle between two stainless-steel plates spaced 1 cm apart in a vacuum of 5×10^{-6} Torr. The upper field plate has a stainless-steel-screen-covered hole to allow the collection of ions in a particle multiplier tube which sits above the plates. A dc voltage or a pulse of up to 700 V with a rise time⁸ of 40 ns can be applied to the lower plate. These fields serve in some cases to ionize the molecules and in all cases to accelerate the ions formed to the particle multiplier for detection. The flight time of the ions allows the separation of isotopic species of Li_2^+ , Li^+ , and contaminant ions. The multiplier signal is captured with a gated integrator set to accept that part of the time-resolved ion signal of interest, and the output of the integrator is recorded with an x - y recorder.

Autoionization spectra taken via the $v'=4$ state bandhead with small static fields are shown in Figs. 2(a) and 2(b). The bandhead consists of states with the total angular momentum $J=2-6$. In these initial experiments we have used the bandhead instead of the resolved high- J states, because for high J the P , Q , and R transitions of the Rydberg excitations are well split and mask the Rydberg structure apparent in Fig. 2. In Fig. 2 each Rydberg state appears as a group of lines, due primarily to our use of the bandhead in the B state. For simplicity we shall refer to the group as a state. Our spectra have the same appearance as those obtained by McGeoch and Schlier,⁹ who used essentially the same excitation method; however our vibrational assignments differ by 1. They assigned the transitions as $\Delta v=0$, whereas other work^{10,11} has shown that for low- v' levels of the B state, $\Delta v=v^*-v'=-1$

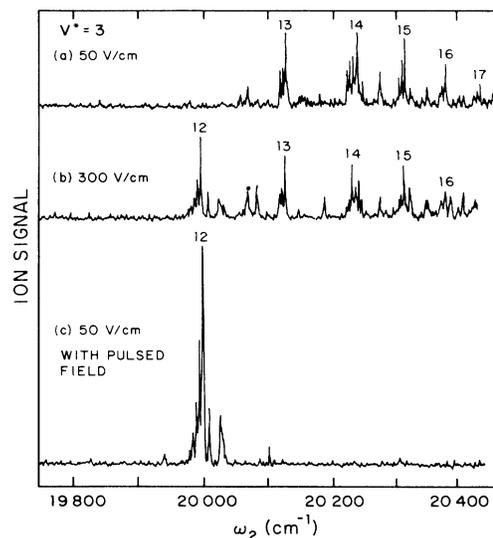


FIG. 2. Autoionization spectra with $v^*=3$ excited via the $v'=4$ B state bandhead. (a) A dc electric field of 50 V/cm is applied, and a Rydberg series starting with $n=15$ is observed. The peaks are composite mainly due to the fact that several J' states in the bandhead are excited and therefore several J^* peaks also appear. Other peaks, possibly due to a different Rydberg series also appear. (b) The dc field is increased to 300 V/cm, and the $n=12$ state appears because of forced autoionization. (c) A dc field of 50 V/cm and a pulsed field of 700 V/cm delayed 1.25 μs from the laser are applied. The combination of fields separates in time signals from the true autoionizing states from those due to forced autoionization. Only the forced autoionization signal is shown here, confirming that $n=12$ is normally a bound state.

transitions are strongly favored. Thus the observed series in Fig. 2 is a $v^*=3$ -Ry series with a quantum defect of 0.7. When the static field is increased from the 50-V/cm field used to record Fig. 2(a) to the 300-V/cm field used to record Fig. 2(b) the next lower Rydberg state $n=12$ appears. The $n=12$ state is apparently bound in a field of 50 V/cm but not in one of 300 V/cm, in spite of the fact that a field of 300 V/cm is almost 2 orders of magnitude too small to ionize a pure $n=12$ state. Furthermore, we note that increasing the field from 50 to 300 V/cm does not qualitatively affect the autoionizing $n > 12$ states and that the $n=12$ state is not qualitatively different from the higher-lying states. All of these observations are precisely what is expected of forced autoionization of the (12,3) state in a field of 300 V/cm. One point that we might reiterate is that the strong propensity for $\Delta v = -1$ transitions, i.e., from $v'=4$ to $v^*=3$, effectively rules out the direct excitation of the $v^*=0$ continuum (or $v^*\neq 3$ states generally) in this energy range, and the presence or absence of a small electric field does not alter this fact.⁵

In Fig. 2(c) we show a spectrum over the same frequency range, but with a 50-V/cm static electric field combined with a 700-V/cm-field pulse which occurs 1.25 μs after the laser pulses. This technique isolates the normally bound (in 50 V/cm) $n=12$ state from the autoionizing $n > 12$ states. The flight time to the detector of ions from the au-

toionizing $n=13$ states is longer than that of ions produced by pulsed field ionization of the $n=12$ state. Figure 2(c) is the pulsed field ionization spectrum showing only the $n=12$ state. The autoionization spectrum is identical to Fig. 2(a). Note that the $n=12$ spectra of Figs. 2(b) and 2(c) are very nearly the same. Some differences are to be expected due to field effects on energies and lifetimes, but in essence this result is consistent with the similarity of the $n > 2$ states in Figs. 2(a) and 2(b). We have also explicitly measured the (12,3) state lifetime by delaying the field ionization pulse, finding a lifetime of $1.0(2) \mu\text{s}$. This is comparable to the purely radiative lifetime of an atomic $n=12$ state,¹² which implies that predissociation has a negligible rate.

The spectra shown in Fig. 2 and their consistency with expectations based on Fig. 1 are not unique but rather general. For example, as expected on the basis of Fig. 1, excitation of the (14,2) state leads to spectra analogous to those shown in Fig. 2. Similarly, the lifetime is found to be $1.4(3) \mu\text{s}$.

Figure 2 and analogous spectra are clearly consistent with forced autoionization to the Stark-induced continuum associated with the lowest rotational-vibrational state of Li_2^+ . A more precise check is to measure the threshold field for this process. Accordingly, we have measured the threshold fields for ionization of the central peaks of the (14,2) and (12,3) levels by varying the static field, as shown in Fig. 3. The observed threshold fields are given in Table I. We can compare these fields to the fields expected on the basis of ionization to the lowest rotational-vibrational levels of Li_2^+ and to the $J=4$ level, corresponding approximately to dipole autoionization. Taking the $J'=4$ states of the $v'=3$ and 4 vibrational levels of the B state to be dominantly populated in the excitation, we can use their term energies¹³ 21 355 and 21 600 cm^{-1} and the energy of the second laser photon to determine the term energies of Table I for the (14,2) and (12,3) states. These term energies in conjunction with an ionization limit yield binding energies, and finally ionization fields. Using the ionization potential reported by Bernheim, Gold, Tip-ton, and Konowalow,¹¹ which is consistent with a revised

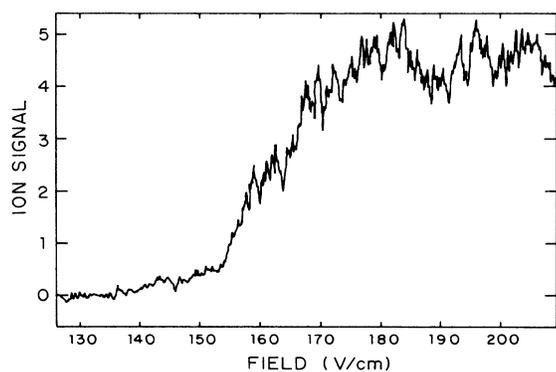


FIG. 3. dc field ionization threshold for the $n=12, v^*=3$ -Ry state. The laser frequencies were fixed on the resonance while the dc voltage on the field plates was varied. The plate spacing was increased to $2.38(8) \text{ cm}$ when these data were taken.

interpretation of the results of McGeoch and Schlier,⁹ we arrive at $41671(4)$ and $41681(4) \text{ cm}^{-1}$ as the $v^*=0$, $J^*=0$, and $J^*=4$ Li_2^+ ionization limits. In Table I we give the calculated ionization fields assuming that forced autoionization occurs in the Stark-induced continua based on these limits. As shown by Table I, the observed fields match almost perfectly the fields calculated for forced autoionization into the $v^*=J^*=0$ state of Li_2 , but are far lower than the fields calculated for forced autoionization to the $J^*=4$ state. Thus we conclude that forced autoionization occurs into any available continua, irrespective of the transfer of angular momentum from Li_2^+ to the departing electron. We have found this to hold up to $J \sim 20$.

The preceding discussion makes it clear that for a series converging to high vibrational limits of Li_2^+ ionization occurs by forced autoionization not by direct field ionization, and that it is the effect of the field on the series converging to the lowest Li_2^+ rotational-vibrational limit which is the determining factor. This realization allows the resolution of an apparent contradiction in the previous Li_2 work. Bernheim *et al.*¹¹ pointed out that the ionization potential given by McGeoch and Schlier⁹ was in error because of the misassignment of the transitions as $\Delta v=0$. However, they did not explain how it was possible to see apparently autoionizing $n=12$ states [our (12,3) states] below the ionization limit. It is clear that it was due to forced autoionization. McGeoch and Schlier used a voltage pulse of 2.2 kV, which, if applied across a plate separation of even as much as 10 cm, would depress the ionization limit enough to observe both the (12,3) and (14,2) states, as reported.

What we have described up to this point implies that forced autoionization will occur if energetically possible, irrespective of the amount of angular momentum transferred. This implies a sharp threshold field for forced autoionization, such as we have shown in Fig. 3. However, as was shown by Eisel and Demtröder,¹⁴ some truly autoionizing states of high J increase in autoionization rate with field, and precisely the same phenomenon can be expected to occur in forced autoionization. The origin of the field dependence of the autoionization rate is that autoionization of a high- J state to the lowest rotational state of Li_2^+ requires a large transfer of angular momentum from the Li_2^+ to the departing electron, a process which is likely to be weak. Thus if only autoionization to the lowest rotational state of Li_2^+ is energetically allowed, the autoionization or forced autoionization rate is slow. However, increasing the electric field both depresses limits relative to

TABLE I. Term energies and observed and calculated ionizing fields.

State	Term energy (cm^{-1})	Observed ionizing field (V/cm)	Calculated ionizing field (to $J=0$) (V/cm)	Calculated ionizing field (to $J=4$) (V/cm)
(14,2)	41 582(3)	218(9)	216(24)	267(29)
(12,3)	41 595(3)	161(8)	157(21)	201(27)

higher rotational levels below the state in question, and destroys the angular momentum of the Rydberg electron as a good quantum number. Both effects reduce the angular momentum transfer required, raising the autoionization rate. The latter effect has been discussed by Eyler.¹⁵

Although it is clear that much systematic work needs to be done, this work shows clearly that field ionization in di-

atomic molecules in most cases occurs by forced autoionization and may be easily understood in those terms.

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*Present address: Battelle-Northwest Laboratory, Richland, WA 99352.

†Present address: Schlumberger-Doll Research, Ridgefield, CT 06877.

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