Electric field effects in the photoionization of N_2 near threshold

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Structural features well below the usual Stark field depression of the ionization threshold are observed in the photoionization of N_2 in the presence of weak (10–15 V/cm) fields. The energies of the structural features can be simulated by assuming rotational autoionization ($\Delta J = -2$). They are interpreted as originating from Q (J'') transitions, forbidden to spontaneously autoionize in the absence of a field. The field relaxes the rigorous autoionization selection rules by l spoilage of the Rydberg electron. The effect appears accentuated for high J, low n^* states ($J \sim 27, 28$; $n^* \sim 23$) and quenches at $J \sim 11$, $n^* \sim 37$. The quenching is attributed to the onset of the Inglis–Teller effect.

I. INTRODUCTION

In tunable VUV photoionization experiments, it is often observed that the measured threshold for ionization occurs at slightly lower photon energy than the value obtained by other methods, e.g., extrapolation of Rydberg series. Various reasons are offered for this depression of the ionization threshold, including collisional, electric field and thermal (Boltzmann population) effects. Recently, several publications have focused on the effects of electric fields, which are almost always used to extract ions or electrons from the region of photoionization.

One such effect, commonly referred to as field ionization, manifests itself in both atoms and molecules. The effect of the Stark field penetrating into the Coulomb field can be treated classically,[1,2] and leads to the equation

$$\Delta E = a \sqrt{F}, \qquad (1)$$

where ΔE is the depression in the ionization threshold, and F is the applied field. With ΔE in cm^{-1} and F in kV/cm, the constant a is 193 for atomic hydrogen. Values of a of about this magnitude have been observed for benzene,[3] napthalene,[4] N_2^+ ($B\,^2\Sigma_u^+$),[5] N_2^+ ($X\,^2\Sigma_g^+$)[6] and the alkalis.[7]

Another phenomenon, obviously applicable only to molecules, is referred to as field-induced rotational autoionization. To our knowledge, pure rotational autoionization (i.e., in the absence of a field) has been observed only in H_2.[8] However, field-induced rotational autoionization has recently been reported for Na_2[9] and Li_2[10,11] in which large changes in angular momentum are observed. Mahon, Janik and Gallagher[11] have formulated a mechanism for this process, involving a sequence of quadrupole transitions, and presented an approximate calculation to support this premise which agrees with their observations.

We have recently reexamined the near-threshold photoionization of N_2, and observed somewhat unusual behavior. Below, we describe the observation, and our interpretation of this behavior.

II. EXPERIMENTAL METHOD

The essential apparatus, consisting of a 3 m normal incidence vacuum ultraviolet monochromator (McPherson) and quadrupole mass spectrometer (Extranuclear Associates) has been described previously.[12] The light source for these experiments was the Hopfield continuum of helium. The dc electric field was produced by a potential applied to the repeller, relative to the case of the ionization chamber. The wavelength resolution for most of the experiments was 0.14 Å (FWHM). Several scans were performed at higher resolution, 0.035 Å (FWHM), in order to resolve the undulatory behavior.

III. EXPERIMENTAL RESULTS

The dependence of the shape of the near-threshold region in the photoionization of N_2 at room temperature is shown in Fig. 1. At low values of the repeller voltage ($F \approx 1$ V/cm) a smooth decline to the background level is observed. As the field is increased, this smooth function moves slightly to lower energies. In addition, an extended ionization region becomes manifest, almost like a step, continuing to significantly lower photon energies. These experiments, performed with the coarser (0.14 Å FWHM) resolution, have been repeated at several pressures between ~ 0.1–1 mTorr. The aforementioned behavior appears to be independent of pressure, and hence collisional effects are not involved.

At higher resolution (0.035 Å FWHM) undulations can be readily observed at the lower photon energies with $F = 13.3$ V/cm [Fig. 2(b)] which are barely perceptible with $F = 0.8$ V/cm [Fig. 2(c)]. The residual effects in the latter experiment could not be tested for pressure dependence, due to the weak signal. Hence, the undulations with $F = 0.8$ V/cm could be due to (a) residual field effects; (b) collisional effects; or (c) weak spontaneous autoionization (see Sec. IV B).

IV. INTERPRETATION OF RESULTS

A. Simulation of experiment

We have tried to simulate the observations, assuming that the effect of the field is to induce rotational autoionization. In this simulation, the rotational Boltzmann population (including nuclear spin statistics) was evaluated at 298 and 78 °K. The transition probability to various Rydberg states was scaled as if the transitions were hydrogenic,
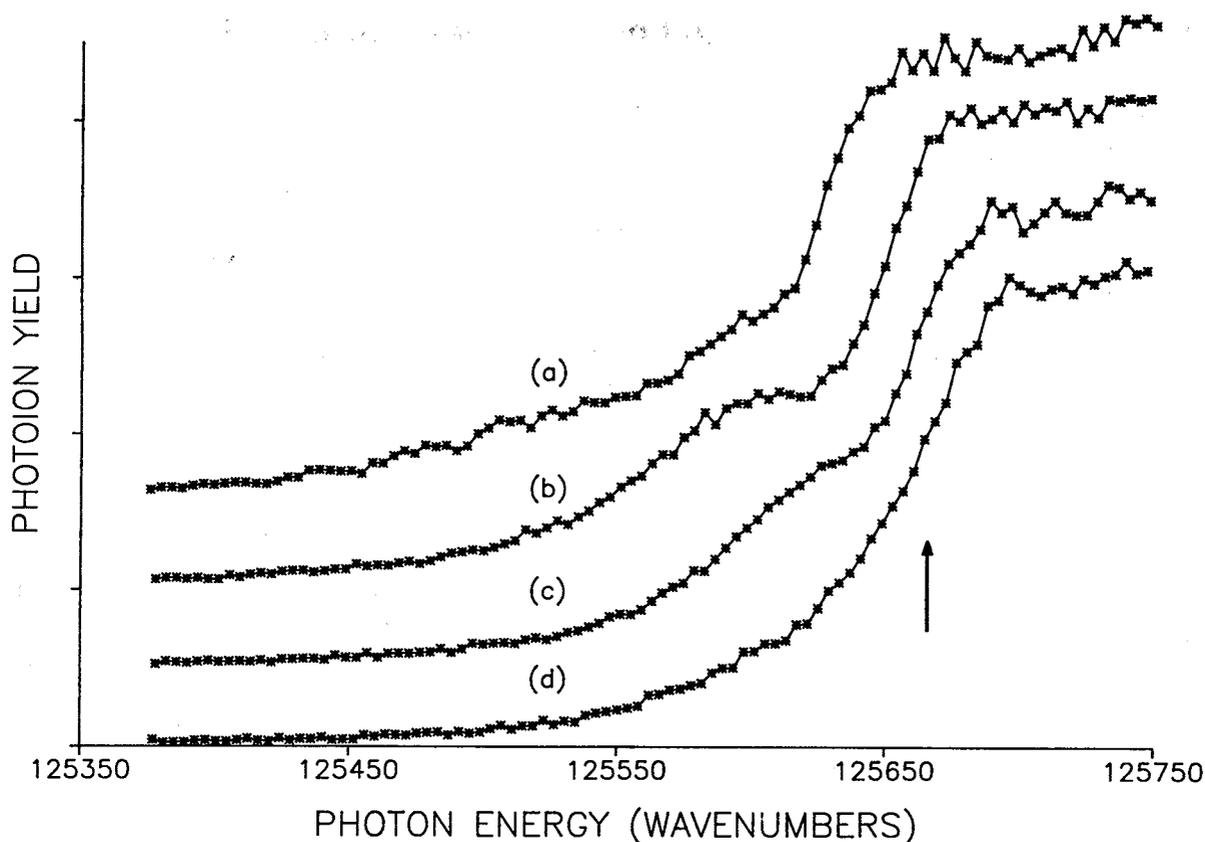
FIG. 1. The influence of weak electric fields upon the photoionization probability below the zero-field ionization threshold in N_2, indicated by the arrow. The photon resolution is 22 cm^{-1} (FWHM). (a) 53.3 V/cm; (b) 13.3 V/cm; (c) 3.3 V/cm; (d) 0.8 V/cm.

i.e., with relative intensities varying as $(n^*)^{-3}$, and independent of the rotational state. Only the Q branch [corresponding to $N^+ = J''$ in Hund's (d) case, where N^+ is the rotational quantum number of the ion core] of each transition was included, with its Hönl–London factor. The basis for this is the prevailing evidence which suggests that the Rydberg electron is primarily p-like, and that the "p complex" coalesces[13] to a rather sharp structure at higher values of n^*. The lowest order autoionizing rotational transition which can be expected is quadrupole, in which two units of rotational angular momentum (and the corresponding energy) are transferred to the Rydberg electron. The energy criterion for rotational autoionization is thus limited to Rydberg states converging to N^+, but lying above the threshold for $N^+ - 2$. The rotational constants that enter are those of the Rydberg states (assumed to be equal to that of N_2^+, $X\,^2\Sigma_g^+$) and the ground state of N_2. It is assumed in this simulation that all Rydberg states meeting the energy criterion can autoionize completely during the experimental lifetime (~ 1–2 μs). The intensities of all of the possible transitions (through $J'' = 28$) are then convoluted with a Gaussian function of half width 0.035 Å, which corresponds to the experimental resolution. The resulting function is displayed in Fig. 2(a).

The simulation is in surprisingly good agreement with experiment at the lowest energies, i.e., between 125 400

and 125 570 cm^{-1}, just before the onset of the plateau in Fig. 2(b). The undulations in the simulation occur at the same energies as they do in the experimental spectrum (taking 125 666.8 cm^{-1} as the adiabatic ionization potential[14] of N_2). The amplitude of the undulations is larger in the experimental spectrum than in the simulation between 125 400 and 125 450 cm^{-1}. This corresponds to $N^+ = J'' = 27,28$ for $n^* \sim 23$ and $N^+ = J'' = 25,26$ for $n^* \sim 24$. Between 125 570 and 125 650 cm^{-1}, the experimental curve falls well below the simulation. This corresponds to a range of lower J states and associated higher n^* states. At still higher photon energies very near to the ionization threshold, normal Stark depression of the ionization threshold is observed.

Thus, three domains appear to be present: (1) a field-induced rotational autoionization, (2) a quenching of this effect, and (3) the normal Stark depression, with a constant "a" close to that in atomic hydrogen. To explain these domains, we first estimate the autoionization rate in the absence of a field, and then examine the influence of the field.

B. Theoretical description

Two formal descriptions for describing rotational autoionization have been proposed, which we shall examine in turn.
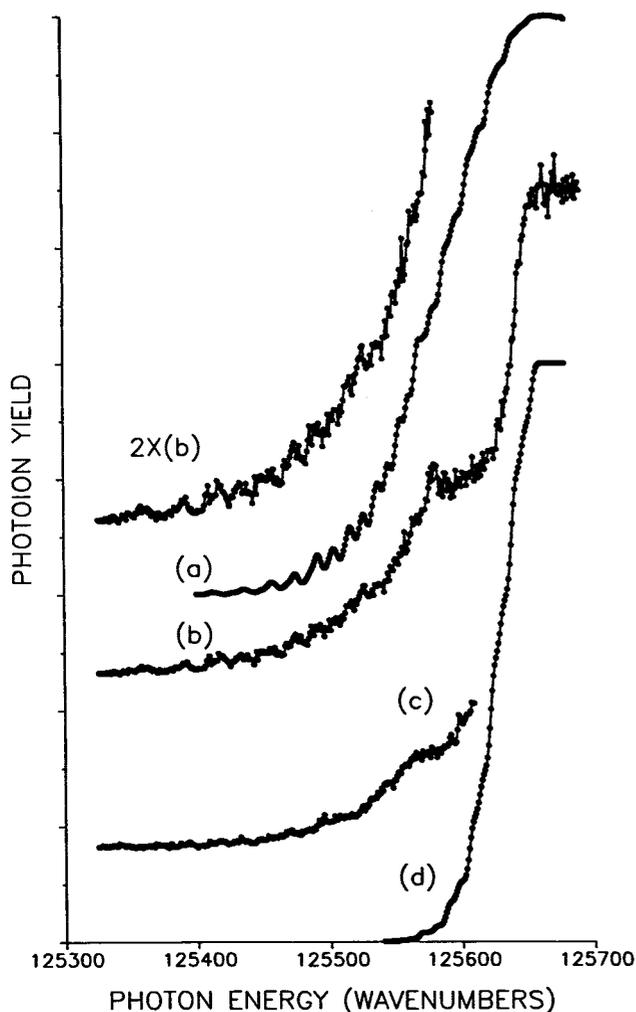
FIG. 2. (a) A simulation assuming that rotational autoionization with $\Delta N^+ = -2$ becomes completely allowed with a weak field. The rotational Boltzmann temperature is taken as 298 K. The other parameters utilized are described in the text. The calculated intensities are convoluted with a Gaussian (half width $= 5.5$ cm^{-1}) to correspond to the experimental resolution. (b) The experimental photoionization yield of N$_2$, with an electric field of 13.3 V/cm and a photon resolution of 5.5 cm^{-1} (FWHM). (c) The same as (b), but with an electric field of 0.8 V/cm. (d) The same as (a), but with a Boltzmann rotational temperature of 78 K.

1. The l-uncoupling approach

In this approach, rotational autoionization is a consequence of the mixing that occurs due to l uncoupling, or going from Hund's case (b) to case (d) coupling. It has been thoroughly discussed for H$_2$,[15,16] but applies equally well to one photon excitation in N$_2$ and Li$_2$, since in all three instances the initial state is $^1\Sigma_g^+$, the final ionic state $^2\Sigma_g^+$, and the Rydberg electron is p-like. In this description, photoabsorption at lower energies excites an electron to $np\sigma$ or $np\pi$ levels, and hence molecular states characterized as $^1\Sigma_u^+$ and $^1\Pi_u$ [Hund's case (b)]. At higher photon energies, the Rydberg electron with $l = 1$ couples to the rotational axis [Hund 's case (d)]. If the rotational angular momentum quantum number of the core in the excited state is N^+, the total angular momentum
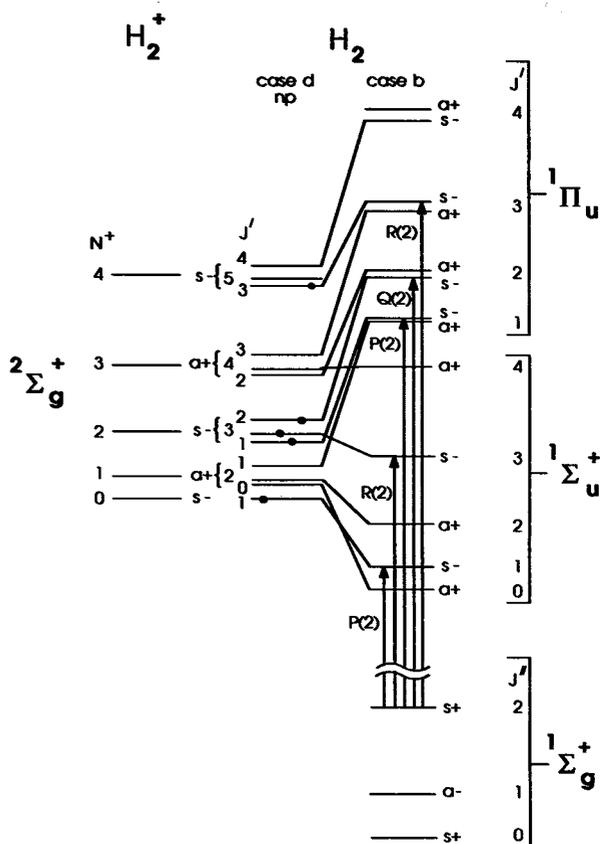
FIG. 3. Schematic diagram showing P, Q and R branches in photoabsorption from $J'' = 2$ in Hund's case b, the correlation to Hund's case d, and the resulting final rotational state of the ion. The diagram illustrates how the two $R(2)$ transitions transform into $np2$ and $np4$ in Hund's case d. Their interaction results in rotational autoionization. A similar effect can occur for the two $P(2)$ transitions, but $Q(2)$ is unique, and cannot rotationally autoionize in the absence of an electric field. The diagram is shown for H$_2$, but should apply as well to N$_2$, Li$_2$ and other alkali dimers.

$J' = N^+ + 1$, N^+, $N^+ - 1$. If alternatively, the core has $N^+ + 2$, then $J' = N^+ + 3$, $N^+ + 2$, $N^+ + 1$. Thus, the levels corresponding to N^+ and $N^+ + 2$ have one value of J' in common ($N^+ + 1$), and these two levels can interact. The ionization limit of Rydberg series with an $N^+ + 2$ core is higher than those with an N^+ core by $2B(2N^+ + 3)$. In this gap there will be Rydberg members with an $N^+ + 2$ core which can mix with the continuum having an N^+ core, providing the mechanism for rotational autoionization. However, there are certain symmetry restrictions for homonuclear molecules, which we shall now consider.

The situation applying to H$_2$, with initial state $J'' = 0$, has been extensively discussed.[15,16] Here we wish to consider a slightly more general case, $J'' = 2$. The dipole selection rules for photoabsorption permit five transitions in Hund's case (b) (see Fig. 3), i.e., $R(2)$ and $P(2)$ for $np\sigma_u$, and $R(2)$, $Q(2)$ and $P(2)$ for $np\pi_u$. Both $R(2)$ transitions obviously have $J' = 3$, and in Hund's case (d) they belong to $N^+ = 3 + 1 = 4$ and $N^+ = 3 - 1 = 2$. We shall refer to these states as $np4$ and $np2$ (or, in general, npN^+). The photoabsorption matrix elements to these states are linear combinations of the photoabsorption matrix elements for $np\sigma$ and $np\pi$. Herzberg and Jungen[16] discuss the

method of calculating these transition amplitudes. From these considerations,

$$D_{np4} = \frac{2}{\sqrt{7}} D_{np\sigma} - \sqrt{\frac{3}{7}} D_{np\pi},$$

$$D_{np2} = \sqrt{\frac{3}{7}} D_{np\sigma} + \frac{2}{\sqrt{7}} D_{np\pi} \qquad (2)$$

where the D's correspond to photoabsorption matrix elements. Furthermore, since in this case $D_{np\sigma} = \sqrt{1/3}$, and $D_{np\pi} = 2/3$, we obtain $D_{np4} = 0$, and $D_{np2} = \sqrt{7}/3$.

In terms of our earlier discussion, there can be transitions to Rydberg levels lying higher than the $N^+ = 2$ limit, which converge to the $N^+ = 4$ limit and interact with the $N^+ = 2$ continuum. However, the photoabsorption probability to these Rydberg states is zero. This is just the condition ($q \sim 0$ in Fano's parametrization[17]) for describing a window resonance.

Such window resonances have been observed particularly between $np2$ and $np0$ in H_2.[16,18,19] However, the above considerations apply quite generally for these systems, i.e. $D_{npJ''+2} = 0$, $D_{npJ''} = \sqrt{2J''+3}/3$. In other words, the spontaneous rotational autoionization resulting from transitions $J'' \to J' = J'' + 1$, $N^+ = J'' + 2$ will lead to window resonances for H_2, Li_2 and N_2. A similar calculation applied to the P transitions leads to a rather different conclusion. In this case, $D_{npJ''} = \sqrt{2J''-1}/3$, and $D_{npJ''-2} = 0$. The implication is that Fano's q will be large, and hence spontaneous autoionization consequent upon the photoabsorption process $J'' \to J' = J'' - 1$, $N^+ = J''$, $J'' \geqslant 2$ will give rise to peaks rather than windows. This inference is not yet confirmed by experiment. The $P(1)$ lines (the only relevant P transitions identified[16]) are much weaker than the $Q(1)$ lines, and in any event, $P(1)$ transitions cannot autoionize.

The Q transitions are unique. Since Q transitions cannot occur to $np\sigma$, but only to $np\pi$, there is no σ-π mixing. Consequently, there is almost no perturbation in a Q Rydberg series.[16] Hence, spontaneous autoionization cannot result from such transitions. However, as is well known, a Stark field mixes l values. This effect negates the rigorous autoionization selection rules implicit in the above discussion, and can enable the Q-like transitions to find autoionization pathways. Since the Q transitions are dipole allowed, and in fact are the strongest transitions, they are very likely the origins of the field-induced autoionization peaks observed in N_2.

To complete this discussion, we note that the spontaneous autoionization width (or rate) is given by[8]

$$\Gamma = 2\pi \frac{2R}{(n^*)^3} \frac{J'(J'+1)}{(2J'+1)^2} (\delta_\pi - \delta_\sigma)^2. \qquad (3)$$

This width is weakly J' dependent, and is quite narrow for the n^* values encountered in the present study. If it corresponds to a window resonance, it would be difficult to observe, either because of resolution restrictions near threshold, or because of a very weak continuum farther below threshold. However, the theoretical considerations

described above would imply that, in principle, both spontaneous and field-induced rotational autoionization should be occurring.

2. The quadrupole coupling approach

Eyler and Pipkin[20] have shown (in case d coupling) how V, the interaction of the Rydberg electron with the molecular ion core, can be evaluated by a multipole expansion for a homonuclear diatomic molecule. Thus,

$$V = \sum_{\text{core}} \frac{e_{\text{Ryd}} e_{\text{core}}}{|r - r_{\text{core}}|} = V_Q$$
$$+ \text{ higher order even multipoles}, \qquad (4)$$

where

$$V_Q = \sum_{\text{core}} e_{\text{core}} r_{\text{core}}^2 \cdot C_0^{(2)}(\text{core}) \cdot \frac{e_{\text{Ryd}}}{r^3} C_0^{(2)}(\text{Ryd}),$$

where $\Sigma_{\text{core}} e_{\text{core}} r_{\text{core}}^2 C_0^{(2)} = Q$ is the quadrupole moment of the molecular ion core.

The separation of V into core and Rydberg electron coordinates ($r_<$ and $r_>$) is permissible in the absence of core penetration by the Rydberg electron. For the present case, where $l = 1$, this condition is not satisfied. However, Mahon et al.[11] note that in atomic autoionization, where similar expressions have been used, the autoionization rates for low l states where penetration does occur are roughly equal to the rate of the lowest l nonpenetrating state. Thus, we use $l = 3$ in subsequent calculations.

Eyler and Pipkin[20] express the matrix element, including the product of spherical harmonic tensors, in 6-j and 3-j symbols, as follows:

$$H_Q = \langle nNlJM_J | V_Q | \epsilon' N'l'J'M_J' \rangle$$

$$= Q \cdot \left\langle nl \left| \frac{1}{r^3} \right| \epsilon'l' \right\rangle \cdot$$

$$(-1)^{l+N'+J} \begin{Bmatrix} J & N' & l' \\ 2 & l & N \end{Bmatrix} \delta_{J,J'} \delta_{M_J,M_J'}$$

$$\times (-1)^l [(2l'+1)(2l+1)]^{1/2} \begin{pmatrix} l' & 2 & l \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times (-1)^{N'} [(2N'+1)(2N+1)]^{1/2} \begin{pmatrix} N' & 2 & N \\ 0 & 0 & 0 \end{pmatrix}, \qquad (5)$$

with selection rules $\Delta J = 0$, $\Delta M_J = 0$, $\Delta N = 0, \pm 2$, $\Delta l = 0, \pm 2$.

Here, N is the core rotational angular momentum quantum number, (for the sake of simplicity, the superscript $+$ has been omitted from N^+), l is the orbital angular momentum of the Rydberg electron, J is the vector sum of N and l, and M_J its projection on the rotational axis. The unprimed symbols refer to the Rydberg state, and primed symbols to the ionization continuum.

The hydrogenic matrix element for a bound–free transition has been approximated by Mahon et al.[11] for a continuum wave normalized per unit energy as follows:

$$\left\langle nl \left| \frac{1}{r^3} \right| \epsilon'l \right\rangle = \frac{1}{n^{3/2}} \cdot \frac{1}{(l+1/2)^3} \qquad (6)$$

$$\left\langle nl \left| \frac{1}{r^3} \right| \epsilon' l + 2 \right\rangle \cong \frac{1}{30} \cdot \frac{1}{n^{3/2}} \cdot \frac{1}{(l+5/2)^3}. \tag{7}$$

We shall evaluate the matrix elements for a typical rotational level which exhibits structure, $J'' = 22$.

For the $\Delta l = 0$, $\Delta N^+ = -2$ case, the angular factor has an average value of ~ 0.15. The appropriate hydrogenic matrix element, with $n^* = 26.3537$, amounts to 1.72×10^{-4}. With a quadrupole moment of N_2^+ of ~ 1.72 a.u.,[21] the total matrix element becomes 4.45×10^{-5}. From the golden rule expression

$$\Gamma = 2\pi |H_Q|^2, \tag{8}$$

we obtain a rate $\Gamma = 1.24 \times 10^{-8}$ a.u., or 5.14×10^8/s.

For the $\Delta l = +2$, $\Delta N^+ = -2$ case, the angular factor has an average value of ~ 0.14, and the hydrogenic matrix element is 1.48×10^{-6}, resulting in a total matrix element of 3.56×10^{-7}. The rate Γ becomes 7.99×10^{-13} a.u., or 3.30×10^4/s. Thus, these calculations imply that the $\Delta l = 0$ transition should be observable in the absence of a field, but the $\Delta l = +2$ transition should not be observable, since the residence time of the Rydberg state in the region of ion extraction is a few microseconds.

This approach does not distinguish between P, Q and R transitions. We have seen (Sec. IV B 1) that P and R autoionization transitions can occur spontaneously with $\Delta l = 0$, but the Q absorption lines required l spoiling to undergo autoionization.

It is interesting to compare the golden rule rate expressions that result from the two approaches [i.e., Eq. (3) and Eq. (8)]. Both expressions involve $(n^*)^{-3}$, a weak J dependence, and a measure of the departure from sphericity of the molecular ion core. In the l-uncoupling approach, this asphericity is contained in the term $(\delta_\pi - \delta_\sigma)^2$, while in the quadrupole coupling approach, it is implicit in the magnitude of $|Q|^2$. For the example considered above $(J'' = 22, n^* = 26.35)$, the autoionization rate obtained by the quadrupole approach is lower than that from the l-uncoupling approach by a factor ~ 35. Perhaps coincidentally, the two rates become more nearly equal if $l = 1$ in Eq. (6).

C. The "Inglis–Teller domain"

With the application of a small field (~ 10 V/cm), the $\Delta N^+ = -2$ transitions are observed between approximately $N^+ = J'' = 28$, $n^* \approx 23$ and $N^+ = J'' = 17$, $n^* \approx 30$, but appear to be quenched at $n^* > 37$. Even in the absence of a field, both calculations indicate that the autoionization rate (when permitted by selection rules) diminishes at higher n^*, as $(n^*)^{-3}$. However, in the presence of a field, another effect may manifest itself for these higher Rydberg states. The polarizability of a Rydberg atom or molecule increases as n^6. The electric field will induce an electric dipole moment, separating the positive (core) and negative (Rydberg electron) charges. The angular velocity of molecular rotation for N_2 ($J = 17$) is about an order of magnitude faster than the angular velocity of the Rydberg electron ($n = 30$). Under such circumstances, the induced

dipole moment will align itself with the field, and the molecular ion will rotate while the dipole moment, and hence the Rydberg electron, precesses about the electric field axis. This behavior should decrease the induced rotational autoionization, both because the Rydberg electron is farther (on the average) from the molecular ion core, and because the Stark effect mixes l quantum numbers, and quantizes m_l instead. If only very low values of m_l are effective in field induced autoionization, this dilution of effective l states introduces another factor n, so that $\Gamma \propto n^{-4}$.[22]

To meet the above criterion, the applied field should be large enough to significantly influence successive Rydberg levels, but not large enough to force them into the ionization continuum. The Inglis–Teller limit[23] meets this requirement. It is the field at which n and $n + 1$ levels overlap, and hence are no longer spectrally resolved. They are converted into a quasicontinuum, but are not yet ionized. This field is given by

$$F \cong 17.1 \times 10^8/n^5 \tag{9}$$

with F in V/cm.

With $F = 13.3$ and 53.3 V/cm (Fig. 1), the Inglis–Teller limit occurs at $n \sim 42$ and $n \sim 32$. At higher n values, the field effectively captures the Rydberg electron, quenching the field induced autoionization. However, such fields can depress the ionization threshold only to $n \sim 70$ (13.3 V/cm) and $n \sim 50$ (53.3 V/cm), which are then the onsets of the weaker field induced ionization.

The apparent enhancement of rotational autoionization at high J'' (27,28) compared to the simulation, and in fact the gradual decline of rotational autoionization with decreasing J'', compared to the simulation, could be attributable to the decreasing quadrupole coupling as J'' decreases, and hence n^* increases. The field induced rotational autoionization would be very difficult to observe at 78 °K [see the simulation in Fig. 2(d)] since only relatively low J values are populated.

V. CONCLUSIONS

Most photoionization experiments are conducted in the presence of at least a weak field, to extract photoions and/or photoelectrons. Under these conditions, the ionization threshold is lowered (for atoms and molecules) weakly by $\Delta E(\text{cm}^{-1}) = aF^{1/2}$, where F is in kV/cm and a is about 190. For N_2, and presumably other homonuclear diatomic and molecules, a weak field can lower the ionization threshold by a larger amount, due to field induced rotational autoionization of high J states. According to our analysis, a symmetry selection rule which prevents spontaneous rotational autoionization of levels populated by $Q(J'')$ transitions is relaxed in the presence of the field, due to l spoiling.

Such an effect is observable in N_2 at fields of ~ 10–15 V/cm between $N^+ = J'' = 28$, $n^* \approx 23$ and $N^+ = J'' = 17$, $n^* \approx 30$, but barely perceptible at a field of ~ 1 V/cm. For higher values of n^* (lower values of J), the effect is quenched. Our inference is that higher n^* states are more

strongly influenced by the field, in such a way as to diminish the induced rotational autoionization. The transition region occurs at about the Inglis–Teller limit.

ACKNOWLEDGMENT

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