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TWO-COLOR STUDIES OF AUTOIONIZING STATES OF SMALL MOLECULES

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Two-color, resonantly enhanced multiphoton ionization (REMPI) is proving to be a valuable technique for the study of autoionizing states of small molecules. In this talk, results obtained by combining REMPI, photoelectron spectroscopy, and mass spectrometry will be discussed and will be illustrated by examples from our recent studies of rotational and vibrational autoionization in molecular hydrogen and rotational autoionization in nitric oxide.

For the study of pure rotational autoionization in H_2, the first laser was used to pump the selected two-photon E,F $^1\Sigma_g^+$, v'=E0, J'=0-4 ← X $^1\Sigma_g^+$, v"=0, J" transition, and the second laser was used to probe transitions to levels in the region of the H_2^+ X $^2\Sigma_g^+$, v^+=0, $\bar{N}^+$ thresholds. These studies were performed by monitoring the low energy photoelectron signal. The $2s\sigma_g$ character of the inner (E) well of the E,F $^1\Sigma_g^+$ state leads to the selective excitation of np Rydberg states with the probe laser; Rydberg states with other values of ℓ are not observed.

Figure 1 shows the spectrum obtained by pumping the Q(2) transition to the E,F $^1\Sigma_g^+$, v'=E0, J'=2 level. From a consideration of the electric dipole selection rules,[1] one expects five allowed np Rydberg series: a J=1 series converging to $\bar{N}^+$=0 (labelled P(2)np0), three series with J=1,2, and 3 converging to $\bar{N}^+$ =2 [labelled P(2)np2, Q(2)np2, (or, more conventionally, Q(2)npπ) and R(2)np2, respectively] and a J=3 series converging to $\bar{N}^+$=4 (labelled R(2)np4). The P(2)np0 series gives rise to a weak J=1 continuum above the $\bar{N}^+$=0 threshold, and the other J=1 series, P(2)np2, undergoes rotational autoionization by coupling with this continuum. Above the $\bar{N}^+$=2 threshold, the three np2 series give rise to a strong continuum. In this region, the weak R(2)np4 series couples with the strong R(2)np2 continuum, giving rise to a series of window resonances. The rotational

autoionization of the J=2 and J=3 series below the $\bar{N}^+$=2 threshold is more problematic, as there are no allowed singlet, εp continua for X $^2\Sigma_g^+$, v^+=0, $\bar{N}^+$=0. This difficulty can be overcome for the J=3 series if one postulates p-f Rydberg-Rydberg or Rydberg-continuum interactions, as the X $^2\Sigma_g^+$, v^+=0, $\bar{N}^+$=0 + εf continuum has J=3. Because competing decay mechanisms (i.e., fluorescence and predissociation) are slow, it is estimated that p-f mixing of as little as 0.05% could account for the observed decay.[1] Similarly, one can account for the decay of the J=2 series if one postulates singlet-triplet mixing between channels, as there is a triplet X $^2\Sigma_g^+$, v^+=0, $\bar{N}^+$=0 + εp continuum with J=2. It is estimated that a singlet-triplet mixing as small as 1 part in 10^6 could account for the observed decay.[1] Thus, REMPI studies of rotational autoionization are seen to be effective probes of extremely weak interactions.

Two-color REMPI was also used to probe Rydberg states of NO converging to the first ten rotational levels of NO^+ X $^1\Sigma^+$, v^+=0 using the A $^2\Sigma^+$, v'=0 intermediate state. Above the $\bar{N}^+$=0 threshold, rotational autoionization of Rydberg series converging to higher thresholds is observed. In contrast to H_2, predissociation of the Rydberg states of NO is found to compete with rotational autoionization in much the same manner as predissociation competes with vibrational autoionization in the region of the first few vibrational levels of NO^+ X $^1\Sigma^+$.[4,5] Aside from a scaling factor of $1/n^3$, the predissociation rate is expected to vary slowly in the wavelength region of the present study, and, in particular, it is not expected to change significantly as the probe laser is scanned through an $\bar{N}^+$ threshold. Thus, predissociation provides an approximately constant decay rate to which the rotational autoionization rates for different values of ΔN^+ can be compared. Because NO is a heteronuclear molecule, rotational autoionization can occur

for both even and odd values of ΔN^+. However, rotational autoionization by $\Delta N^+=2$ is found to be faster than by $\Delta N^+=1$ or 3. This results from the symmetry requirement that ΔN^+ = even processes require interactions between levels that both have even or both have odd values of orbital angular momentum ℓ, while ΔN^+ = odd processes require interactions between levels of which one has even ℓ and the other has odd ℓ. The latter interactions are known to be weak in NO.[2]

In summary, two-color REMPI provides a powerful tool for the study of the photoionization dynamics of autoionizing states.

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References

1. M. A. O'Halloran, P. M. Dehmer, S. T. Pratt, J. L. Dehmer, and F. S. Tomkins, J. Chem. Phys., in press.
2. S. T. Pratt, J. L. Dehmer, and P. M. Dehmer, to be published.

Figure 1. Two-color (2+1') excitation spectrum of autoionizing np Rydberg states of H_2 excited from the E,F $^1\Sigma_g^+$, v'=E0, J'=2 state. The abscissa gives the total energy from the H_2 $^1\Sigma_g^+$, v"=0, J"=0 ground state.

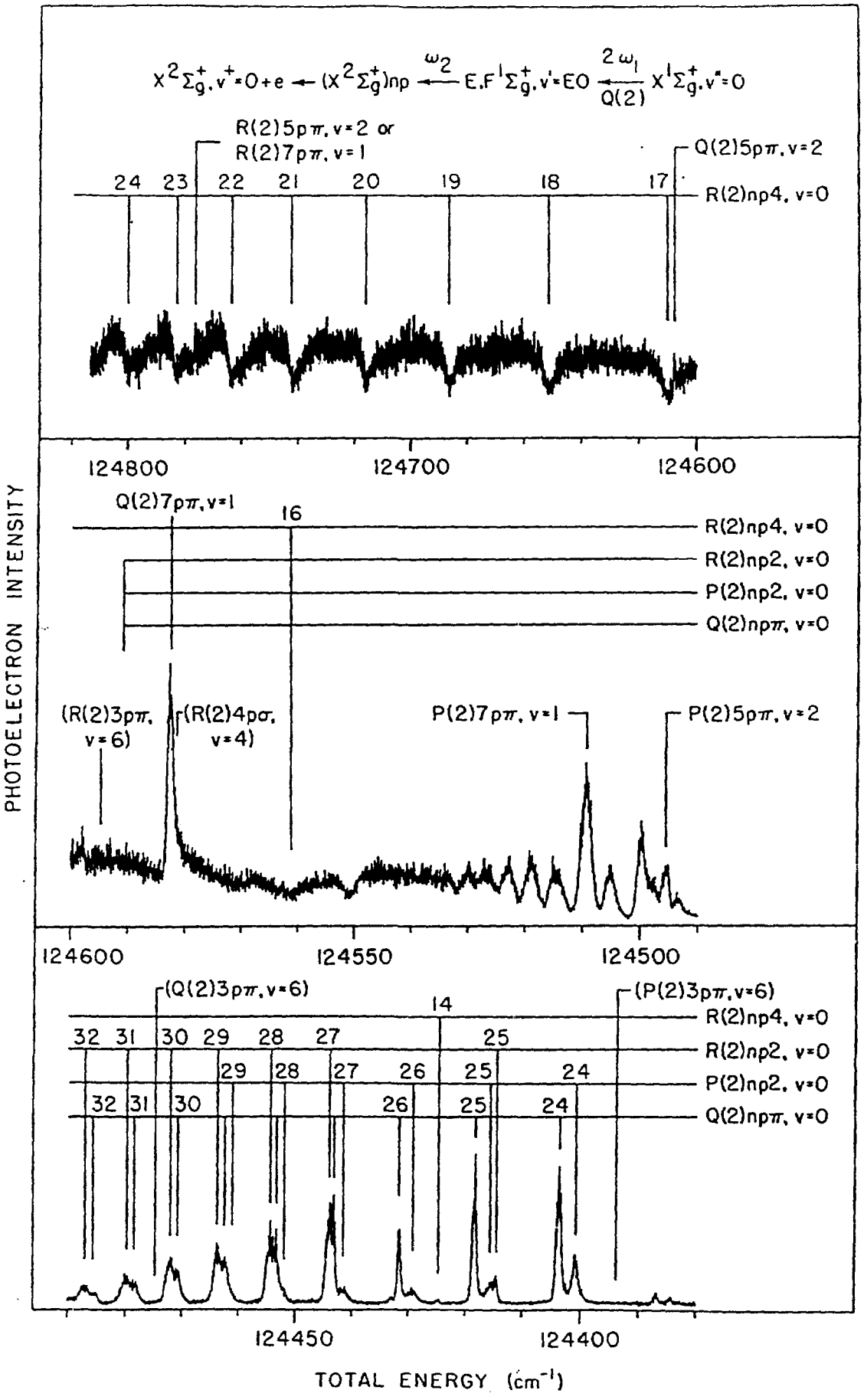
$X^2\Sigma_g^+, v^+=0 + e \leftarrow (X^2\Sigma_g^+)np \xleftarrow{\omega_2} E,F\,^1\Sigma_g^+, v'=E0 \xleftarrow[Q(2)]{2\omega_1} X\,^1\Sigma_g^+, v''=0$
R(2)5pπ, v=2 or
R(2)7pπ, v=1
Q(2)5pπ, v=2
R(2)np4, v=0
24 23 22 21 20 19 18 17
124800
124700
124600
Q(2)7pπ, v=1
16
R(2)np4, v=0
R(2)np2, v=0
P(2)np2, v=0
Q(2)npπ, v=0
(R(2)3pπ, v=6)
(R(2)4pσ, v=4)
P(2)7pπ, v=1
P(2)5pπ, v=2
124600
124550
124500
(Q(2)3pπ, v=6)
14
(P(2)3pπ, v=6)
R(2)np4, v=0
R(2)np2, v=0
P(2)np2, v=0
Q(2)npπ, v=0
32 31 30 29 28 27 25
29 28 27 26 25 24
32 31 30 26 25 24
124450
124400
PHOTOELECTRON INTENSITY
TOTAL ENERGY (cm^{-1})

Figure 4