Advances in Laser Science - III
edited by W.C. Stwalley and
M. Lapp (American Institute of
Physics, New York, 1988).

# VIBRATIONAL AUTOIONIZATION AND FANO-ANTIRESONANCE IN RYDBERG SERIES OF NAPHTHALENE

JACK A. SYAGE AND JOHN E. WESSEL

The Aerospace Corporation
P.O. Box 92957
Los Angeles, CA 90009

*ABSTRACT*

Asymmetric Fano-line profiles have been observed by autoionization for specific vibrational excitation of Rydberg series in jet-cooled naphthalene. The line shapes were analyzed in terms of degenerate resonance interference between optically active discrete and continua states. Observed linewidths were as narrow as 6 $cm^{-1}$ for naphthalene and 3 $cm^{-1}$ for naphthalene-$d_8$.

## *INTRODUCTION*

In recent years, multiphoton excitation studies in molecular beams have revealed the presence of well-resolved molecular autoionizing Rydberg states in large molecules[1-3]. In each case, the autoionization spectra consisted of relatively sharp and symmetric transitions superimposed on an otherwise continuous background. In the present work, we report clear evidence of asymmetric Fano line profiles observed in autoionizing Rydberg series of jet-cooled naphthalene[4]. These unusual lineshapes, referred to as antiresonances, occur by degenerate resonance interference of a discrete state with a continuum when both carry oscillator strength from a common initial or intermediate state[5].

## *RESULTS AND ANALYSIS*

Our pulsed supersonic molecular beam apparatus and time-of-flight (TOF) mass spectrometer have been described in detail elsewhere[6]. Briefly, the output of two independently tunable dye lasers are frequency doubled to generate $\omega_1$ and $\omega_2$. Naphthalene was introduced into a differentially pumped molecular beam apparatus via a pulsed supersonic nozzle heated to 70°C and under 40 psi He. Two-photon ionization signals arising from one-color excitation by the laser scanning $\omega_2$ were suppressed by operating a shutter that blocked the $\omega_1$ pulse on alternate triggers. The $\omega_2$ only signal was then subtracted from the $\omega_1+\omega_2$ signal, providing the signal-to-noise ratio required to resolve the weak Rydberg series superimposed on the continuua.

A vibrationally selected autoionizing excitation spectrum is presented in Fig. 1 for a region above the adiabatic ionization level, $IP_o$. Excitation by $\omega_1$ to the $\bar{8}^1 7^1$ nontotally symmetric combination vibration of $S_1$ followed by $\omega_2$ excitation reveals a strong Rydberg series, $R_n$, converging to the presumed $^+\bar{8}_1 7_1$ ionization threshold at 1537 $cm^{-1}$ (versus 1422 $cm^{-1}$ in $S_1$). Additional structure is evident in Fig. 1, which appear to be part of other Rydberg series. The prominence of the $R_n(\bar{8}^1 7^1)$ series by $\omega_2$ excitation is indicative of a propensity for $\Delta v = 0$ transitions. Excitation of the totally symmetric $7^1$ vibration of $S_1$ (at 988 $cm^{-1}$) by $\omega_1$ followed by $\omega_2$ excitation

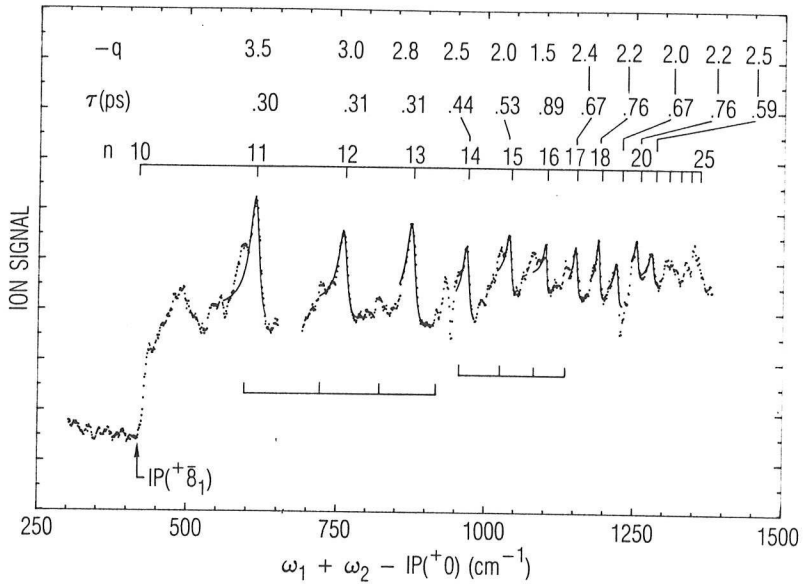


*Figure 1.* Double resonance autoionization spectrum of napthalene recorded via the intermediate state $S_1(\bar{8}^1 7^1)$. The energy scale is relative to the vertical ionization potential at 65665 $cm^{-1}$. A major Rydberg series is identified and Fano lineshape analysis represented by the best-fit values for $q$ and $\tau$(ps). Parts of two other Rydberg series are identified but not assigned.

gave a similar Rydberg series for $7^1$. Other transitions were studied that did not include $\nu_7$ in $S_1$, however no Rydberg autoionization was observed. The autoionizing features in Fig. 1 were fitted to the n=11 to 21 members of a Rydberg series that converges to $IP_o$ + 1537 $cm^{-1}$ and has a quantum defect of $\delta = .10$. The low value of $\delta$ is consistent with a $d$ series, which in turn is consistent with the large transition moment from the $S_1(\pi, \pi*)$ intermediate state if we consider a qualitative $\Delta l = 1$ selection rule.

The involvement of a smooth ionization continuum in the present case allows us to use a simple formulation[5] of Fano's original theory for the antiresonance lineshape $L(\epsilon)$;

$$L(\epsilon) = \frac{(q+\epsilon)^2}{(1+\epsilon^2)}$$

$$\epsilon = 2\hbar(\omega - \omega_o)/\Gamma \quad ; \quad q = \frac{A\mu_{SR}}{|A|\mu_{Sj}V_{Rj}}$$

where $\omega$ and $\omega_o$ are the excitation and line center frequency, respectively; $\Gamma$ is the spectral linewidth. The line profile index $q$ consists of the transition dipole moments from the intermediate $S_1$ level to the Rydberg $R_n$ and continua $j$ states, $\mu_{SR}$ and $\mu_{Sj}$, respectively; the cosine of the angle between the transition dipole vectors, $A$; and the discrete continua interaction responsible for the vibrational autoionization, $V_{Rj}$. Calculated Fano-line profiles are superimposed onto the observed data in Fig. 1 and the best fit values for $q$ and the lifetime $\tau = (2\pi\Gamma)^{-1}$ are reported for each member of the Rydberg series $R_n$.

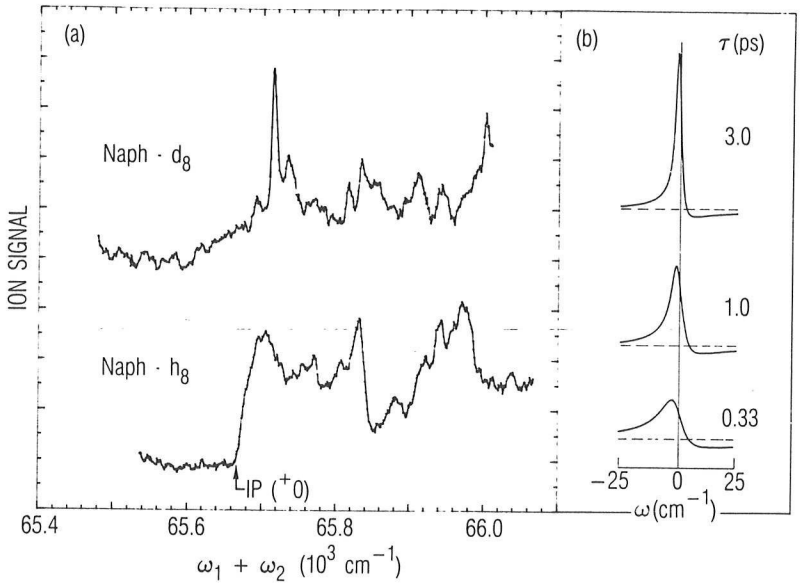


*Figure 2.* (a) Double resonance autoionization spectra recorded via the intermediate state $S_1(7^1)$ for napthalene-$d_8$ ($\omega_1 = 32957$ cm$^{-1}$) and naphthalene-$h_8$ ($\omega_1 = 33014$ cm$^{-1}$). (b) Calculated lineshapes are illustrated as a function of the relative change in the coupling term $V_{Rj}$. Variations in $V_{Rj}$ are represented by the parameter $\tau$(ps) ($\propto 1/V_{Rj}^2$).

The effect of varying the coupling term $V_{Rj}$ was observed by recording autoionizing excitation spectra for naphthalene-$d_8$. A portion of the spectrum for specific excitation of the $R_n(7_1)$ series is presented in Fig. 2. The most evident features are lineshapes that are narrower and more symmetric than those observed for naphthalene-$h_8$. These effects are due to weaker vibrational-electronic coupling and are in accord with the predictions of the Fano-model described above. The relative change in the antiresonance lineshape is illustrated in Fig. 2 for variations in the value of $V_{Rj}$. The observed linewidth of 4 cm$^{-1}$ for the major feature in Fig. 2 corresponds to an autoionization time of greater than 1.3 ps. (Linewidths as narrow as 3 cm$^{-1}$ have been measured for other lines.) This time is undoubtedly larger if we take into account the rotational broadening ($\sim$ 2 cm$^{-1}$) inherent in our expansion conditions.

## *REFERENCES*


1. J. Hager, M. A. Smith, and S. C. Wallace, *J. Chem. Phys.* **84,** 6771 (1986).
2. A. Goto, M. Fujii, and M. Ito, *J. Phys. Chem.* **91,** 2268 (1987).
3. M. Fujii, T. Kakinuma, N. Mikami, and M. Ito *Chem. Phys. Lett.* **127,** 297 (1986); T. Suzuki, N. Mikami, and M. Ito, *Chem. Phys. Lett.* **120,** 333 (1985); M. Fujii, N. Mikami, and M. Ito, *Chem. Phys.* **99,** 193 (1985).
4. J. A. Syage and J. E. Wessel, *J. Chem. Phys.*, **87,** 6207 (1987).
5. U. Fano, *Phys. Rev.* **124,** 1866 (1961); J. Berkowitz, *Photoabsorption, Photoionization, and Photoelectron Spectroscopy,* (Academic Press, New York, 1979).
6. (a) J. A. Syage and J. E. Wessel, *J. Chem. Phys.* **87,** 3313 (1987); (b) J. A. Syage and J. E. Wessel, *Appl. Opt.* **26,** 3573 (1987).