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Citation: The Journal of Chemical Physics **110**, 9961 (1999); doi: 10.1063/1.478869 View online: http://dx.doi.org/10.1063/1.478869 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/110/20?ver=pdfcov Published by the AIP Publishing

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# Vibrational predissociation dynamics in the vibronic states of the aniline-neon van der Waals complex: New features revealed by complementary spectroscopic approaches

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(Received 29 October 1998; accepted 3 March 1999)

We report two independent sets of experimental spectroscopic data which both contain information about the vibrational dynamics occurring in the aniline-neon van der Waals complex in its  $S_1$ electronically excited state. The high resolution excitation spectra of the three vibronic bands,  $\overline{6a_0^1}$ ,  $\overline{I_0^2}$ , and  $\overline{1_0^1}$ , of the  $S_1 \leftarrow S_0$  transition, exhibit lifetime broadening with respect to transitions to the corresponding states in the aniline monomer. The dispersed emission spectra taken under excitation of the same three vibronic bands give access to both the distribution of aniline monomer states produced by vibrational predissociation of the complex and to the rates at which this dynamics proceeds. The overall results are discussed in a consistent way, with emphasis being given to the role of the coupling between the intramolecular and the intermolecular vibrational states. In the case of  $\overline{I_0^2}$  excitation, it is shown that this coupling is reflected in the shape of the van der Waals wavefunction, as accessed through the analysis of the high resolution spectra [M. Becucci, G. Pietraperzia, N. M. Lakin, E. Castellucci, Ph. Bréchignac, Chem. Phys. Lett. **260**, 87 (1996).]. © 1999 American Institute of Physics. [S0021-9606(99)01020-X]

#### I. INTRODUCTION

What governs the outcome of intramolecular dynamics in a large system has been a central question in chemical reaction dynamics for many years. The search for evidence of mode specificity has known little success, in spite of many efforts to interrogate molecular systems by spectroscopic techniques, both in the frequency and in the time domain.<sup>1</sup>

The study of van der Waals (vdW) clusters is of fundamental interest for the understanding of detailed intramolecular dynamics, as these species can be considered as model systems in which the reduction in magnitude of both the binding strength and vibrational frequencies induces a general reduction of the dynamical rates, without preventing efficient unimolecular reactions from taking place. The timescale of these internal processes may reach the nanosecond range, making them particularly accessible to study using high resolution spectroscopic techniques. Over such time intervals, the internal dynamics competes with radiative processes in the excited states of many molecules. This situation can be turned into a means to measure reaction rates by comparing the relative intensities which can be observed in the various reactive channels to that in the main radiative channel.

In the present work we have studied the first electronic transition in the aniline-neon vdW complex in the nearultraviolet using the complementary techniques of laser excitation spectroscopy at high resolution and dispersed emission spectroscopy. These methods provide jointly a fairly complete description and understanding of the dynamical behavior of the molecular system when the intramolecular vibrational modes in the first electronically excited state of the vdW complex are excited. On the one hand, the measurement of the linewidths in the high resolution excitation spectra give direct information on the excited states lifetimes. On the other hand, the measurement of the branching ratios for the various final states following vibrational excitation in dispersed emission spectra give the vibrational predissociation rates, thanks to the internal molecular clock provided by the natural lifetime of the free molecule. In addition, high resolution excitation spectroscopy provides information about the molecular structure of the complex in the states involved in the transition. This structure reflects the averaging of the inertial tensor over the vibrational motions of the complex in a particular vibronic state. In cases of favorable symmetry it has been used to provide a measure of the quantum mechanical extension of the large amplitude internal motions in the complex.<sup>2</sup> In particular a measure of the amplitude of the vdW bending motion of aniline-neon in the lowest vibrational levels of the  $S_0$  and  $S_1$  electronic states was reported in a previous article.<sup>3</sup> Consequently the high resolution spectroscopy of higher-lying excited vibronic

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states of this vdW complex offers a unique way to interrogate the heart of the quantum reaction dynamics.

The use of various excitation energies, as resulting from allowed intramolecular vibronic transitions in aniline, opens the possibility to explore a wider range of the vdW potential energy surface than was allowed from the spectra of the origin transition<sup>3</sup> only. Indeed the vdW surface associated with an excited intramolecular vibration lies above the vdW surface associated with the  $0^0$  state, and due to the coupling between intermolecular and intramolecular modes both surfaces affect the wavefunction. This coupling is responsible for a time-dependent vibrational dynamics, whose rate is even more sensitive than the wavefunction to the relative shapes of these surfaces at the common excitation energy. When the excitation energy exceeds the vdW binding energy vibrational predissociation may proceed towards the energetically allowed product channels. The relative partial rates determine the branching ratios.

Three different vibronic bands of aniline, namely the  $6a_0^1, I_0^2$ , and  $1_0^1$  bands, have been used to investigate in detail the vibrational dynamics induced by the preparation of the corresponding vibrational states in the aniline-neon cluster. The rate for vibrational predissociation (VP) exhibits a marked sensitivity to the exact nature of the intramolecular mode that is prepared. Of particular interest is the observed correlation between the enhancement of the predissociation rate, when the inversion mode of aniline is excited, and the extension of the corresponding quantum wavefunction revealed by the high resolution excitation spectroscopy.

The layout of this paper is as follows: Sec. II summarizes the main aspects of the experimental procedures, Sec. III describes the results obtained independently by the two techniques, and Sec. IV compares, discusses, and interprets these data on the basis of the present knowledge of intramolecular dynamics.

#### **II. EXPERIMENT**

The high resolution fluorescence excitation and the dispersed fluorescence experiments were performed, respectively, at the LENS laboratory in Florence and at the LPM in Orsay. Both experiments have already been described elsewhere;<sup>4,5</sup> here we will give only a short summary.

The high resolution spectrometer at LENS is formed by the combination of a collimated supersonic molecular beam and a cw single mode ring dye laser (with intracavity doubling of the fundamental frequency to reach the near-UV). The gas mixture (0.1% aniline in pure neon) was expanded into the first chamber at a backing pressure of 600 kPa through a 50  $\mu$  nozzle. The central core of the expansion was collimated by a 400  $\mu$  conical skimmer, placed at 10 mm from the nozzle. The crossing of the resulting molecular beam with the laser beam occurred at 34 cm downstream the skimmer, where the total undispersed fluorescence was imaged onto a cooled photomultiplier (EMI 9893Q/350) and the signal was recorded by photon counting. The absolute frequency of the laser source was monitored (on the fundamental wave) by a wavemeter (Burleigh PWA). The relative frequency shift was calibrated against a pressure-sealed, tem-



FIG. 1. High resolution fluorescence excitation spectrum of the  $6a_0^1$  vibronic band of the  $S_1 \leftarrow S_0$  electronic transition of the aniline–neon van der Waals complex in a continuous supersonic molecular beam.

perature stabilized, Fabry–Perot interferometer of 150 MHz free spectral range (this value was treated as an experimental observable which was accurately determined using the spectrum of the aniline monomer taken immediately after each scan on the vdW complex). The UV laser power was also monitored for the signal normalization. The overall instrumental resolution is 15 MHz, mainly limited by residual Doppler broadening.

The experimental apparatus which has been used in Orsay to spectrally analyze the emission following vibronic excitation of the aniline–neon complex consists of a supersonic free jet crossed by the beam of a pulsed, frequency-doubled, tunable dye laser, pumped by a Q-switched Nd-YAG laser.<sup>5</sup> The laser induced fluorescence (LIF) was collected at right angles by a system of optics which imaged the central part of the jet onto the entrance slit of a grating monochromator (Jobin et Yvon, F=320 mm) and the light emerging from the exit slit was detected by a photomultiplier. The dispersed emission spectra of the species present in the jet (free aniline molecules and vdW complexes) were recorded as a function of wavelength as the stepping motor driving the rotation of the grating was scanned by a microcomputer.

## **III. RESULTS**

### A. High resolution spectroscopy

We report in Figs. 1 and 2 the spectra of the  $\overline{6a_0^1}$  and the  $\overline{I_0^2}$  vibronic bands of the  $S_1 \leftarrow S_0$  electronic transition of the aniline–neon vdW complex. Both spectra, as well as the spectrum of the  $\overline{1_0^1}$  vibronic band (not shown) are extremely similar to the already published spectrum of the  $\overline{0_0^0}$  vibronic band of the complex.<sup>3</sup> The major difference is the presence of a significant line broadening in the  $\overline{I_0^2}$  band, which is the signature of enhanced relaxation in the excited state. All three spectra consist of a superimposition of two different components, which correspond to the two neon-20 and neon-22 isotopic forms of the complex.<sup>3</sup>

All rotational assignments were obtained by simulation and least-squares (LSQ) fits using a rigid rotor Hamiltonian.<sup>6</sup> The number of assignments made for each vibronic band



FIG. 2. High resolution fluorescence excitation spectrum of the  $I_0^2$  vibronic band of the  $S_1 \leftarrow S_0$  electronic transition of the aniline–neon van der Waals complex in a continuous supersonic molecular beam.

depends upon the linewidth of the isolated transitions: this determines both our ability to resolve single eigenstates and the effective signal-to-noise ratio. The  $I_0^2$  band was the most difficult to analyze due to the large linewidth and the possible presence of spectral perturbations. In a first stage of analysis we independently determined both the ground state (g.s.) and the upper state (u.s.) rotational constants for the  $\overline{0_0^0}$ ,  $\overline{6a_0^1}$ , and the  $\overline{1_0^1}$  bands. The values determined for the g.s. were found to be equal within the error of the measurements (see Table I, in which the standard deviation is reported in parentheses, in units of the last digit). To minimize the number of free parameters we have taken advantage of the fact that all these transitions share a common vibronic ground state: we therefore averaged over the three sets of g.s. constants obtained in the independent fits and then fixed them to this new set of values in final LSQ fits of the three bands. The typical deviation between the calculated and the experimental line positions was ca. 8 MHz. The same set of g.s. constants was then used for the analysis of the  $\overline{I_0^2}$  vibronic band, under the assumption that this transition shares the same ground state as the others. The number of assignments we were able to make for the  $I_0^2$  band was limited due to the

TABLE I. Rotational constants on the ground state of the aniline-neon complex obtained in fits of different vibronic bands.

	$\overline{0^0_0}$	$\overline{6a_0^1}$	$\overline{1_0^1}$	Averaged values
Aniline-20N	le			
$A'' (cm^{-1})$	0.061 81(3) <sup>a</sup>	0.061 88(3)	0.061 84(3)	0.061 84(2)
B''	0.057 44(20)	0.057 50(9)	0.057 53(15)	0.057 50(13)
C''	0.043 78(20)	0.043 59(9)	0.043 48(15)	0.043 59(13)
Aniline-22	Ne			
A''	0.060 98(3)	0.061 00(3)	0.061 00(2)	0.061 00(2)
B''	0.055 33(19)	0.055 40(28)	0.055 38(17)	0.055 37(13)
<i>C</i> ″	0.041 70(19)	0.041 90(28)	0.041 88(17)	0.041 82(13)

<sup>a</sup>Numbers given in parentheses represent one standard deviation of the parameter in units of the last quoted decimal place.

linewidth and the resulting lower signal-to-noise ratio. We were able to fit for the neon-20 complex only 24 transitions belonging to the lower *J* "clumps of transitions" and 13 transitions for the neon-22 complex with a 20 MHz standard deviation. Table II reports the u.s. rotational constants for the  $\overline{0_0^0}, \overline{6a_0^1}, \overline{1_0^1}, \overline{and}, \overline{I_0^2}$  vibronic bands of the two isomeric forms of the aniline–neon vdW complex.

The rotational constants determined from an experiment are determined by the inertial properties of the molecular system. Unfortunately the direct inversion of the rotational constants to give the molecular geometry is not always possible, especially in such a loosely bound system as a vdW molecule. In complexes involving an aromatic monomer the weak binding between the rare gas atom and the aromatic ring allows a large freedom for the motion of the rare gas atom in a plane parallel to the ring. The rotational constants of the complex therefore reflect an *effective* value of the molecular geometry and not just the average values of the atom positions.<sup>7</sup>

In order to properly discuss the problem of the aniline– neon complex it is necessary to define a suitable axis system to describe the inertial tensor of the complex. We will assume that the aniline molecule is a rigid body whose geometry is unchanged upon complexation. The reference frame, as already discussed in a previous paper,<sup>8</sup> is attached to the center of mass of the aniline–neon complex so that the axes (x,y,z) are parallel to the principal inertial axes  $(a_0,b_0,c_0)$  of the monomer. The inertial tensor is then given by

$$\begin{pmatrix} k/A_0 + \mu(Y^2 + Z^2) & -\mu XY & -\mu XZ \\ -\mu XY & k/B_0 + \mu(Z^2 + X^2) & -\mu YZ \\ -\mu XZ & -\mu YZ & k/C_0 + \mu(X^2 + Y^2) \end{pmatrix} = \underbrace{\mathbb{M}}_{=} \begin{cases} k/A & 0 & 0 \\ 0 & k/B & 0 \\ 0 & 0 & k/C \end{cases} \underbrace{\mathbb{M}}_{=}^{-1},$$
(1)

where  $A_0$ ,  $B_0$ , and  $C_0$  are the rotational constants of the aniline monomer in the corresponding vibronic state; *X*, *Y*, and *Z* are the coordinates of the neon atom with respect to the aniline principal axes;  $\mu$  is the reduced mass of the complex and the proportionality constant  $k = h/(8\pi^2 c)$  (in units: cm<sup>-1</sup> amu Å<sup>2</sup>); *A*, *B*, and *C* are the calculated rotational

constants of the complex; and M is the unitary transformation matrix between our frame and the principal axes of the complex.

The above tensor was used to derive effective coordinates for the neon atom,  $X_{eff}$ ,  $Y_{eff}$ , and  $Z_{eff}$ , for each vibronic state using the experimentally determined rotational con-

TABLE II. Rotational constants on the  $S_1$  excited states of the aniline–neon complex obtained in fits of different vibronic bands.

	$\overline{0^0_0}$	$\overline{6a_0^1}$	$\overline{I_0^2}$	$1^{1}_{0}$
Aniline-20Ne				
$A' (cm^{-1})$	0.061 38(3) <sup>a</sup>	0.061 36(3)	0.061 57(8)	0.061 39(3)
B'	0.056 72(3)	0.056 71(3)	0.056 84(9)	0.056 72(3)
C'	0.044 32(9)	0.044 30(9)	0.043 32(9)	0.044 30(9)
Aniline-22Ne	e			
A'	0.060 43(2)	0.060 34(3)	0.060 40(10)	0.060 45(3)
B'	0.054 78(3)	0.054 83(3)	0.054 73(20)	0.054 78(3)
С'	0.042 51(9)	0.042 49(9)	0.041 83(20)	0.042 51(9)

<sup>a</sup>Numbers given in parentheses represent one standard deviation of the parameter in units of the last quoted decimal place.

stants. These effective coordinates involve some combination of the vibrationally averaged coordinate value and the amplitudes of the vibrational motion. Nevertheless in some special cases, when symmetry makes the mean value of a coordinate equal to zero, or when the mean value of a coor dinate is, in absolute terms, very much larger than its vibrational amplitude, it is possible to determine one or the other of these quantities. Both symmetry considerations (all of the excited vibronic states are of A' type in  $C_S$  group) and the shape of the potential well for the rare gas atom demand that the mean value of Y is zero. Therefore we have direct access with  $Y_{\rm eff}$  to a measure of the root-mean-square deviation of the vibrational motion along this coordinate, denoted  $\Delta Y$ . The mean distance between the neon atom and the aromatic ring (typically ca. 3.4 Å)<sup>8</sup> is much larger than the expected amplitude of the vibrational wavefunction in this direction (typically ca. 0.1 Å),<sup>9</sup> so that the value  $Z_{eff}$  we determine (for Z) basically reflects the former value. Finally the yz plane is not a symmetry plane of the complex and therefore the mean value of X will be nonzero, so it is almost impossible to separate in  $X_{\rm eff}$  the contributions from the mean value of X and from the vibrational amplitude  $\Delta X$ .

In order to calculate the effective coordinates,  $X_{eff}$ ,  $Y_{eff}$ , and  $Z_{eff}$ , from the experimental rotational constants we built a grid of values for X, Y, and Z. We then calculated for each possible set of values the rotational constants via Eq. (1) and we accepted only those values that reproduced the rotational constants to within tolerable limits. Finally we averaged over

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TABLE III. The effective coordinate sets obtained from the experimental rotational constants for all the vibronic states of aniline $-^{22}$ Ne.

	$S_0^{a}$		$S_{1}$						
	$\overline{O_0}$	$\overline{0^0}$	$\overline{6a^1}$	$\overline{I^2}$	$\overline{1^1}$				
$X_{\rm eff}$ $Y_{\rm eff}$	0.209(2) <sup>b</sup> 0.249(39)	0.218(1) 0.203(14)	0.216(1) 0.227(10)	0.187(11) 0.586(44)	0.220(1) 0.311(18)				
$Z_{\rm eff}$	3.399(1)	3.378(1)	3.372(1)	3.373(6)	3.375(1)				

<sup>a</sup>Determined from averaged values of rotational constants.

<sup>b</sup>Numbers given in parentheses represent the range of acceptable solutions in units of the last quoted decimal place.

all the acceptable sets of coordinate values. The calculated values of  $X_{eff}$ ,  $Y_{eff}$ , and  $Z_{eff}$  and the range of acceptable values, for each vibronic level and for the ground state, are reported in Table III. For reasons which were discussed in Ref. 3 (i.e., the proximity of the aniline–<sup>20</sup>Ne complex to a symmetric top and the resulting interchange of inertial axes occurring along the vdW stretching coordinate), only the values for aniline–<sup>22</sup>Ne are significant for our analysis and will be used in the forthcoming discussion.

Once the spectra were fully assigned it was possible to measure the linewidth for each single rovibronic transition and to determine the line center position. We fitted the experimental lineshape using a Voigt profile. The Gaussian component was fixed to our known instrumental resolution<sup>4</sup> while the Lorentzian part was a free parameter. Table IV contains the fitted Lorentzian widths,  $\gamma_i$ , together with their standard deviations for each of the vibronic bands of the complex, and the Lorentzian widths,  $\gamma_0$ , for the corresponding vibronic bands in the aniline monomer, already measured in our laboratory.<sup>10</sup> The linewidth is independent of the eigenstate rotational quantum number in the region from J''=0 to 3. The  $I_0^2$  band represents a special case: due to the low S/N ratio and the large linewidth, the analysis was limited to the R(1) "clump" (see Fig. 3). The lines with higher rotational quantum numbers are strongly superimposed and a line profile analysis was not possible. Table IV also contains the positions,  $\nu_i$ , of both the vdW complex and the monomer<sup>10</sup> vibronic bands, and the pure vibrational vdW shifts,  $\delta_i$ . The latter are defined as the changes of the vibra-

TABLE IV. Band origins and linewidths (FWHM) measured for the vibronic bands of the  $S_1 \leftarrow S_0$  transition of aniline–neon compared to their values in the free molecule. The pure vibrational vdW shifts are also given.

Vibronic band	$\overline{0^0_0}$	$\overline{6a_0^1}$	$\overline{I_0^2}$	$\overline{1_0^1}$	
Band origins $\nu_i$ (cm <sup>-1</sup> ) <sup>a</sup>					
vdW complex (this work)	340 24.17(3) <sup>b</sup>	345 16.76(3)	347 85.60(3)	348 22.52(3)	
monomer (Ref. 10)	340 29.26(3)	345 21.70(3)	347 90.06(3)	348 27.15(3)	
Vibrational shifts $\delta_j$ (cm <sup>-1</sup> )	0.0	0.15(4)	0.63(4)	0.46(4)	
FWHM (MHz)					
vdW complex $\gamma_i$ (this work)	18(2)	39(3)	138(10)	48(4)	
monomer $\gamma_0$ (Ref. 10)	18(2)	18(2)	18(2)	18(2)	

<sup>a</sup>Measured for the aniline $^{20}$ Ne vdW complex. The corresponding transition for the aniline $^{22}$ Ne vdW complex is shifted by  $-0.040 \text{ cm}^{-1}$  with respect to that of aniline $^{20}$ Ne.

<sup>b</sup>Numbers given in parentheses represent one standard deviation of the parameter in units of the last quoted decimal place.



FIG. 3. The "R(1) clump of rotational components" in the  $S_1 \leftarrow S_0$   $\overline{0_0^0}$ ,  $\overline{1_0^1}$ , and  $\overline{I_0^2}$ , vibronic transitions of the aniline–neon complex. The Lorentzian linewidth was determined only after deconvolution with a 15 MHz instrumental function.

tional separations induced by the vdW binding (for more information see Sec. IV).

#### **B.** Dispersed emission experiment

Figure 4 shows the dispersed emission spectrum (bottom trace) recorded after excitation of the  $\overline{6a^1}$  level of the vdW complex, together with the assignments of the main bands. It can be seen that in addition to bands corresponding to transitions from the  $\overline{6a^1}$  state of the vdW complex to excited vibrational levels in the ground state of this complex, other features are observed which can be assigned to fluorescent emission involving monomer states. The bands assigned to emissions of the vdW complex are the dominant contributors to the overall emission intensity, which indicates that predissociation proceeds at a slower rate than radiative emission in the complex. One of the most prominent progressions is built upon the  $I^1$  monomer state, which appears to be the preferred fragment channel. The other final fragment states which can be identified are the ground state  $0^0$  and the  $10b^2$  states.



FIG. 4. Dispersed emission spectrum (bottom trace) recorded under excitation through the  $\overline{6a_0^1}$  band of the aniline–neon complex, and example of the reconstruction of this spectrum as a weighted sum of spectra due to various individual excited states (see text).

Figure 4 also shows how the branching ratios of the various final states are quantitatively determined by comparison of the experimental spectrum with a reconstructed spectrum obtained by summing up the properly weighted individual emission spectra expected from the directly excited complex state and from the observed monomer states. Some of these emission spectra can be directly measured, i.e., those originating from all the excited monomer states that can be reached by laser excitation (Franck-Condon and symmetry allowed vibronic bands). This is indeed the case for two of the states produced following excitation of the  $\overline{6a^1}$  level of the complex, namely the state  $0^0$  and the  $10b^2$  states. Unfortunately many open product channels, especially those accessed when the excitation energy is larger, do not correspond to laser accessible monomer states. The  $I^1$  state, prominent in Fig. 4, or states like  $10b^1$ ,  $16a^1$ ,  $16b^1S^1$ , which are formed in the predissociation following the  $\overline{I^2}$  or  $\overline{I^1}$  excitations fall into this category. Such states usually appear in sequence bands in the room temperature spectra, and compilation of the literature data allows us to obtain frequencies and intensities that can be used to build a synthetic stick spectrum (see Appendix).

For the final comparison with the experimental spectrum, the stick spectrum is convoluted at the actual experimental resolution, which depends on the width of the monochromator slits used for the measurements. Visual comparison of the two spectra is used because the spectral congestion becoming rather strong when extending far to the red of the excitation band can cause automated fitting procedures to give unphysical results. We estimate the accuracy of the branching ratios obtained in this way to be of the order of 0.03 for the weak features, and of 10% for the main features. This means that some of the product states formed with low efficiency and responsible for the weakest bands can only be tentatively identified. It is, however, very important in the context of this paper which aims at comparing the total relaxation rate as measured by the lifetime broadening in the high resolution spectra with that deduced from the branching ratios obtained by measuring the dispersed emission spectra, to realize that only the branching ratio for the fluorescence out of the initially excited state matters. For all the bands investigated here, this branching ratio is large, and thus well determined (to about 10% relative accuracy).

The results thus obtained for the branching ratios for fluorescence arising from the initially excited states and of all the final states are summarized in Table V. Measurements were made using excitation through the same three vibronic bands for which high resolution, rotationally resolved spectra had also been recorded, namely  $\overline{6a_0^T}$ ,  $\overline{I_0^T}$ , and  $\overline{I_0^2}$ . Only three final product states were found in the case of  $\overline{6a^1}$  excitation and of these, the  $I^1$  and  $10b^2$  states, which lie within a few tens of wavenumbers of the initially excited complex state (see Fig. 5), represent about 85% of all fragments. The lower lying states  $10b^1$  and  $16a^1$  should be very weak, if at all present, while the ground  $0^0$  state accounts for the remaining 15% of fragments. The fact that neither the  $16a^2$  state, nor the  $10b^116a^1$  combination state, which lie very close to the  $10b^2$  state, were found tends to suggest that either their coupling to the initially prepared state is much weaker than that

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TABLE V. Branching ratios for vibrational predissociation of the aniline–neon complex. Summary of the branching ratios for fluorescence out of the initially excited and all the final states, as derived from the dispersed emission spectra taken under excitation on the  $\overline{6a_0^1}$ ,  $\overline{I_0^2}$ , and  $1_0^1$  bands, respectively. All the energies have been referred to the  $0^0$  monomer state. The value  $D_0 = 142 \text{ cm}^{-1}$  for the dissociation energy was used to set the energies of the complex states relative to this reference.

State	<u>6</u> <i>a</i>	<u>1</u> 0	0	$I^1$	$10b^{2}$						
Energy Branching ratio	35 0.6	0 0 51 0.0	) )6	334 0.23	348 0.09						
State	$\overline{I^2}$	$10b^{1}$	$16a^{1}$	$I^1$	$10b^{2}$	$6a^1$	$I^1 \ 10b^1$	$I^1  16a^1$	$S^{1}  10b^{1}$	$10b^{3}$	$16b^1 \ 10b^1$
Energy Branching ratio	618 0.22	174 0.028	177 0.032	334 0.034	348 0.042	492 0.078	508 0.140	511 0.117 <sup>a</sup>	514 0.102	522 0.085 <sup>b</sup>	561 0.106
State	$1^{1}$	$10b^{1}$	$4^{1}$	64	$I^1$ $I^1$	$10b^{1}$	$S^1 \ 10b^1$				
Energy Branching ratio	656 0.74	174 0.09	365 0.0	5 49 7 0.0	2 )3	508 0.03	514 0.05				

<sup>a</sup>Part of this intensity may be shared with the  $S^1$  state lying at 340 cm<sup>-1</sup>.

<sup>b</sup>Part of this intensity may be shared with the  $16b^{1}$  state lying at 387 cm<sup>-1</sup>.

of the other nearby states, or that they are energetically forbidden. Since the 10*b* and 16*a* modes have already be found to be strongly mixed together and with the vdW modes around 350 cm<sup>-1,5</sup> the latter condition is much more plausible, and would set a lower bound for the dissociation energy at 142 cm<sup>-1</sup>.

The  $10b^1$  is the strongest product channel in the case of  $\overline{I^1}$  excitation, but predissociation proceeds about as slowly as in the case of  $\overline{6a^1}$  excitation. On the contrary it is much more efficient in following  $\overline{I^2}$  excitation. In this case the fragments are distributed among a large number of final states, and the most populated of these product states lie predominantly at high energy (80% of the products are found in states lying above 492 cm<sup>-1</sup>). Also remarkable is the fact that, in spite of a larger excitation energy these highest lying states were not present or were too weakly populated to be observed in the predissociation out of the  $\overline{I^1}$  level.

## **IV. DISCUSSION**

The results presented in the above section need to be discussed in the light of present understanding of intramolecular dynamics and unimolecular processes. More specifically the sets of data originating from the two different ex-



FIG. 5. Scheme of the energy levels involved in the predissociation processes studied in this work.

periments, involving different techniques and different setups, must first be compared to one another, before they can then be commented upon in the framework of the theoretical background specifically available for vibrational predissociation (VP) and intramolecular vibrational redistribution (IVR) in vdW complexes.

In the case of the dispersed emission experiment, the branching ratio  $R^{j}$  for emission from the initially excited state  $|j\rangle$  is a direct measure of the efficiency of the relaxation from this state through IVR and/or VP. We have

$$R^{j} = k_{0} / (k_{0} + K^{j}), \tag{2}$$

in which  $k_0$  is the intrinsic relaxation rate of the free molecule resulting from both radiative and nonradiative transitions (known to be dominated by intersystem crossing in aniline), and  $K^{j}$  is the additional relaxation rate introduced by the vdW dynamics (IVR and/or VP). The value of  $k_0$  will be taken as the inverse of the lifetime of the  $S_1 0^0$  level in aniline. Indeed previous studies have established that the lifetimes for several other vibronic states of the aniline molecule<sup>10</sup> as well as for the  $\overline{0_0^0}$  state of the neon-complex<sup>3</sup> are almost identical (see Table IV). As a matter of fact, both IVR and direct VP channels are open for the relaxation of the vibronically excited  $(S_1 \text{ state})$  vdW complex, and it is of interest to consider the possible competition between the two processes. For the IVR channel to be effective it needs some "dark" states within the observed linewidth. Such states can be divided into bound and unbound states. If bound dark states would be formed, it would affect the dispersed emission spectrum, which has not been seen. If unbound dark states would be formed, they would very quickly (on a picosecond timescale) decay into continuum states, as shown by classical trajectory calculations.<sup>11</sup> However this is very unlikely because the density of states is too small. Indeed a realistic evaluation of the density of vdW states in the ground intramolecular state of  $S_1$ , done by direct count using results of 3D quantum calculations for the frequencies,<sup>12</sup> shows that it cannot exceed 100 states per  $cm^{-1}$  at the highest excitation considered in this work, and the bound dark

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TABLE VI. Summary of the data about relaxation rates out of the various vibronic levels of the aniline-neon complex.

Vibronic band	$\overline{0^0_0}$	$\overline{6a_0^1}$	$\overline{I_0^2}$	$\overline{1^1_0}$
Excitation energy $(cm^{-1})$	0	492	760	798
$R^{j}$ a	1.00	0.61(6)	0.22(3)	0.74(8)
$\gamma_0 / \gamma_j$	1.00	0.46(10)	0.16(3)	0.38(9)
$K^{j}$ (ns <sup>-1</sup> )	0	0.113	0.693	0.168

<sup>a</sup>Numbers given in parentheses represent one standard deviation of the parameter in units of the last quoted decimal place.

states are even sparser. Very likely VP proceeds in aniline– neon prepared in the  $\overline{6a^1}$ ,  $\overline{I^2}$ , and  $\overline{I^1}$  states, through the direct mechanism, which involves coupling of the initially prepared state with the continuum states.

In the case of the linewidth measurements from high resolution excitation spectra the total relaxation rate for an excited state  $|j\rangle$  is given by

$$k_i = 1/\tau_i = 2\pi\gamma_i. \tag{3}$$

Assuming that the increase of the relaxation rate from its value  $k_0$  for the  $\overline{0^0} S_1$  state is entirely due to the IVR and/or VP processes, we have

$$k_j = k_0 + K^j$$
, or, equivalently  $\gamma_i = \gamma_0 + K_i/2\pi$ ,

where  $\gamma_0$  is the FWHM of rotational lines in the aniline  $\overline{0}_0^0$  band. Finally, we obtain

$$R^{j} = \gamma_{0} / \gamma_{j} \,. \tag{4}$$

Table VI contains the independently obtained values of the branching ratios  $R^{j}$  and the ratios  $\gamma_{0}/\gamma_{i}$  for the three initially prepared excited states of aniline-20 Ne which have been studied in both experiments. The overall agreement is satisfactory; it is within the experimental uncertainties for the  $\overline{6a^1}$  and  $\overline{I^2}$  excitations. However, the relaxation out of the  $\overline{I^1}$ state seems to proceed at a slower rate, as measured by the dispersed emission compared to the linewidth measurements. A possible difference between the two kinds of measurements, rather than a mere discrepancy, could result from the influence of a dark channel which depopulates the  $\overline{I^1}$  state. Two possibilities can give rise to this situation. In the first one an actual physical process, such as a relaxation to a nonfluorescent state opens up at an excitation energy slightly smaller than the  $\overline{1^1}$  state energy. The second, more plausible possibility is that the dispersed fluorescence experiment is not capable of detecting all the final states. Indeed, because of spectral congestion which makes data reduction very difficult, not all the spectral range over which fluorescence can be seen has been recorded, but instead preferentially the high frequency side where isolated bands can be unambiguously identified.

The first remark concerning Table VI is that the relaxation rates  $K^j$  [which are equivalent to the increase in the rotational linewidth on complexation,  $2\pi(\gamma_j - \gamma_0)$ ] are all small, i.e., the lifetimes remain in the nanosecond range. No other direct measurement of lifetime with which these results may be compared has been reported for aniline complexes with neon, but the values measured here are of the same orders of magnitude as measured for the aniline–argon vdW complex by Nimlos et al.<sup>13</sup> The most striking feature is that the variation of the rate with excitation energy is not monotonous. This is a strong indication that the vibrational dynamics in these vdW complexes is not governed only by the energetics. On the contrary the specific character of the initially excited mode is essential. In particular the VP/IVR relaxation rate,  $K^{j}$ , of the  $\overline{I^{2}}$  state is almost one order of magnitude larger than that of the  $\overline{6a^1}$  state, or even that of the  $1^{1}$  state. A similar behavior was reported by Zhang et al.<sup>14</sup> in the case of the aniline-argon complex. Thus the coupling of the inversion mode to the various vdW modes should be much larger than for the in-plane symmetric ring modes. This is not physically surprising since both the vdW bending modes and the inversion mode of the aniline monomer involve large amplitude atomic motions that are known to accelerate the IVR process in many molecular systems.<sup>15–18</sup> The amplitude with which the hydrogens of the amino group oscillate along a direction orthogonal to the plane of the ring increases, upon excitation of the inversion mode, from about 0.6 Å in the ground state to 1.1 Å in the  $I^2$ state. Consequently even if its average position is a long distance away from this group, the neon atom should be significantly affected by the resulting change in their mutual interaction. Indeed the degree to which this inversion motion is hindered by the rare gas atoms in the small aniline  $-(argon)_n$  clusters has recently been the subject of a theoretical investigation.<sup>19</sup> From this study we can then expect that the spatial dependence (on X, Y, Z) of the wavefunction for the vdW ground state associated to the intramolecular  $\overline{I^2}$  excitation should look different from that of the corresponding vdW state without intramolecular excitation (i.e., the  $\overline{0^0}$  intramolecular state).

As discussed in the previous section, high resolution spectroscopy gives a kind of direct access to these vdW wavefunctions through the way the instantaneous inverse inertia tensor is averaged over the amplitude of the vdW motions. The relevant results are those of Table IV, giving the values of the effective parameters,  $X_{eff}$ ,  $Y_{eff}$ , and  $Z_{eff}$  for the various vibronic states. An interesting trend appears from the values of  $Y_{\rm eff}$  for the aniline–<sup>22</sup>Ne complex: it increases as the linewidth increases (compare Table III and IV, or see the correlation in Fig. 6). We have already commented in Ref. 3 that, among the three effective coordinates,  $Y_{\rm eff}$ , is the one which provides a measure of an amplitude of the vdW motion. Although the approximation made in using the inertia tensor (1) to reproduce the experimental rotational constants means that a precise physical significance cannot be attached to this coordinate, its value appears to provide a useful indication of the degree of coupling of a particular intramolecular vibrational state to the set of vdW modes.

The question of the relation of this coupling strength to the details of intramolecular dynamics has been widely debated in the literature. In the particular context of the vibrational dynamics of vdW molecules, the connection of relaxation rates to the pure vibrational vdW shifts was first made ten years ago by Weber and Rice.<sup>20</sup> These authors, with the benefit of experimental evidence for a limited IVR process (energy transfer from intramolecular to vdW modes without



FIG. 6. Correlation between the linewidth, large amplitude motions, and frequency shift (squared) for the different vibronic bands in the aniline– neon van der Waals complex.

fragmentation) in the *s*-tetrazine–argon complex,<sup>21</sup> were able to justify on a theoretical basis a proportionality relationship between the IVR rate and the vibrational shift. Let us recall that the pure vibrational vdW shift,  $\delta_j$ , of the intramolecular vibrational state  $|j\rangle$  is defined as the change induced by complexing to a partner in the energy separation between the position of this state and the position of the ground state. It is given by the difference in the vdW shifts of the vibronic transition to level  $|j\rangle$  in  $S_1$  with respect to that of the  $\overline{0}_0^0$ transition:

$$\delta_j = \Delta \nu_j - \Delta \nu_0. \tag{5}$$

Miller<sup>22</sup> suggested a different form for the correlation that exists between the VP lifetimes and the vibrational shift,  $\delta$ , for a number of vdW molecules. He empirically showed that the VP lifetime goes as the inverse of the square of the vibrational shift, or equivalently for the VP rate:

$$K \propto \delta^2$$
. (6)

Le Roy *et al.*<sup>23</sup> later demonstrated that this relationship could be theoretically rationalized for a *direct* VP mechanism on an "everything else being equal" basis. This phrase must be understood in the sense that both VP dynamics and the frequency shift are supposed to be controlled by the same coupling factors. Although this assumption is not obviously valid in every practical case, it is an interesting justification for this correlation. Nonetheless, as recently noted by Oudejans *et al.*,<sup>24</sup> the derivation of relation (6) also implicitly assumes that the density of product states is large enough to prevent energy gap considerations from dominating the dynamics.

It is of interest to examine to what degree this correlation is satisfied by the present data (which seem to demonstrate the importance of the coupling factor). Figure 6 shows the 3-dimensional correlation diagram obtained for  $\delta^2$  versus the linewidth,  $\gamma$ , and versus  $Y_{\rm eff}$ . The correlation coefficient between  $\delta^2$  and  $\gamma$  is 0.93, indicating that, although relation (6) reproduces the general trend in the spectra, it does not accurately represent the details of the IVR/VP dynamics at work in this vdW molecule. Considering the distribution of final states revealed by the dispersed emission experiment (Table V) and the partial rates obtained for each fragment state, the deviations from this simple law are likely to result from the role of the other important factors, namely the energy gap,  $\Delta E$ , and the density of states.

Indeed the exponential energy gap law,<sup>25</sup> or its adaptation as the momentum gap law,<sup>26</sup> represents the first solid theoretical background for the description of VP in vdW molecules. Although its application to the case of aromatic molecules is not an easy task because of the large number of intramolecular modes which can be involved, it is important to consider the role of the energy gap parameter  $\Delta E$ . It appears that the final states involving a small  $\Delta E$  seem to be preferred in the present data. This is very clear in the case of the  $\overline{6a^1}$  excitation, where the two main fragment states  $I^1$ and  $10b^2$  (representing 85% of all fragments) lie within 20  $cm^{-1}$  of the exact resonance (if the vdW binding energy is taken to be  $142 \text{ cm}^{-1}$ , in agreement with the discussion at the end of Sec. III B). It is also the case for the  $\overline{I^2}$  excitation, where the fragment states lying above the  $6a^1$  state (i.e., within 130 cm<sup>-1</sup> of resonance) represent 80% of all fragments. In contrast, in the case of the  $\overline{1^1}$  excitation no fragment state is available very close to resonance (see Fig. 5), which may explain the less efficient relaxation. It may be concluded that the size of the coupling element between the initial state and the vdW coordinates is only one of the factors controlling the VP in the observed states of anilineneon, and that the specific characteristics of the final states must also be taken into account to provide a consistent understanding of the data.

A much better correlation is found between the linewidth,  $\gamma$ , and the effective coordinate,  $Y_{eff}$  (correlation coefficient 0.98). The vibrational vdW shift is basically a quantity specific to the initially excited state, without any dependence on the final fragment states. Obviously nothing is more characteristic of the initially excited state than its wavefunction. We have demonstrated the ability of the high resolution spectra to give information about this wavefunction, through the effective vdW coordinate space (X, Y, Z). Thus, if a correlation between the relaxation rates and the shifts is present, we may also expect a correlation between the  $Y_{\rm eff}$  parameter, measuring purely the amplitude of this wavefunction in the y-direction, and the other two parameters. The occurrence of such correlations among the three sets of data is shown in the 3-dimensional plot of Fig. 6. The overall quality of these correlations is striking. This demonstrates clearly that preparation of the large amplitude inversion mode  $I^2$  state both induces the largest rate for IVR/VP dynamics, and reveals a vdW wavefunction containing the largest admixture of other perturbing states. Although the exact nature of these perturbing states is unknown, scattering wavefunctions outgoing in the y-direction are suggested by the present results, which is consistent with the direct VP mechanism that predicts Lorentzian lineshapes, as observed. This graph nicely illustrates the intrinsic connection of the two findings recalled above, as classically recognized in either the time-dependent approach of nonradiative transitions or the time-independent approach of true molecular eigen states. To our knowledge this is the first time that such a correlation has been experimentally demonstrated.

TABLE VII. Franck–Condon factors of the vibronic bands of the  $S_1 \leftarrow S_0$  transition in aniline.

Transition FC	$0^0_0$ 1.00	$I_2^0 \\ 0.71$	$6a_1^0 \\ 0.45$	$1^0_1_{10}_{10}_{10}_{10}_{10}_{10}_{10}_{$	$12^0_1 \\ 0.28$	$I_2^0 6 a_1^0 0.51$	$12^0_1$ 0.28	$18a_1^0 \\ 0.17$	$6a_2^0$ 0.11	$I_2^0 1_1^0 \\ 0.48$	$13^0_1\\0.17$
Transition FC	$I_1^1 \\ 1.22$	$I_1^1 6 a_1^0 0.72$	$I_3^1$ 0.29	$I_1^1 1_1^0 \\ 0.49$	$I_1^1 12_1^0 0.38$	$I_1^1 18_1^0 \\ 0.32$	$I_1^1 6 a_2^0 \\ 0.30$	$I_3^1 6 a_1^0 0.18$	$I_1^1 13_1^0 \\ 0.38$		
Transition FC	$6a_0^1 \\ 0.67$	$6a_0^1I_2^0$ 0.51	$6a_1^1 \\ 0.31$	$6a_0^11_1^0 \\ 0.40$	$6a_1^1I_2^0 0.40$	$6a_0^112_1^0\ 0.28$	$6a_0^1 18a_1^0 \\ 0.17$	$6a_2^1 \\ 0.88$	$\begin{array}{c} 6a_0^1 I_2^0 1_1^0 \\ 0.31 \end{array}$	$6a_0^113_1^0$ 0.13	
Transition FC	$I_0^2 \\ 0.28$	$I_2^2 \\ 0.75$	$I_0^2 6 a_1^0 0.41$	$I_0^2 1_1^0 \\ 0.34$	$I_2^2 6 a_1^0 \\ 0.60$	$I_0^2 12_1^0 0.28$	$I_0^2 18a_1^0 \\ 0.09$	$I_0^2 6 a_2^0 0.11$	$\begin{matrix} I_4^2 \\ 0.42 \end{matrix}$		
Transition FC	$1^{1}_{0}$ 0.62	$1^{1}_{0}I^{0}_{2}$ 0.28	$1^{1}_{0}6a^{0}_{1}$ 0.42	$1^1_1_{10}_{12}_{11}_{11}_{11}_{12}_{12}_{12}_{12$	$\begin{array}{c}1_{0}^{1}I_{0}^{2}6a_{1}^{0}\\0.31\end{array}$	$1^{1}_{0}12^{0}_{1}$ 0.18	$1^{1}_{0}18a^{0}_{1}\\0.18$	$1^1_06a^0_2\\0.13$	$1^{1}_{1}I^{0}_{2}$ 0.51	$1^{1}_{1}6a^{0}_{1}\\0.34$	

## V. CONCLUSION

We have reported new, original results revealing the efficiencies of VP in three vibronically excited states of the aniline–neon vdW molecule. These data are the high resolution (LIF) excitation spectra of the  $\overline{6a_0^1}$ ,  $\overline{1}_0^1$ , and  $\overline{I}_0^2$  vibronic bands of the  $S_1 \leftarrow S_0$  transition in this complex, and the dispersed emission spectra recorded when the same bands are excited.

From the analysis of the excitation spectra the rotational constants of the vdW molecule are determined, as well as the band origin frequencies and the linewidths of the transitions. These linewidths exhibit a contribution from the relaxation in the excited state, which depends on the nature of the mode being excited. The rotational constants characterize the effective inertia tensor, which contains information not only on the vibrationally averaged position of the neon atom with respect to the aniline frame, but also on the amplitude of the wavefunction along one vdW bending coordinate in the corresponding state.

From the analysis of the emission spectra the branching ratios for the final states which are populated by the relaxation in the excited state have been derived. Vibrational predissociation takes place on a timescale which is comparable or longer than the normal radiative lifetime. From the value of this lifetime, and by comparison between fluorescence intensities from the initial and final states, the predissociation rates have been obtained. A tendency to favor final states at small energy separations from the initial state has been observed.

These results obtained from two independent experimental sources have been compared and found essentially consistent. They demonstrate a clear evidence of actual mode specificity: the predissociation proceeds much faster when the out-of-plane large amplitude inversion motion of aniline is excited at 760 cm<sup>-1</sup>, while excitation of the in-plane symmetric ring vibration mode 1 at 798 cm<sup>-1</sup> only shows the normal general increase of the rate k(E) versus energy. This finding is recognized to be connected to the unusual strength of the coupling of this out-of-plane mode with either the bath of the vdW modes or the density of the continuum states built upon each final state channel. Indeed, under the assumption that this coupling strength is reflected by the value of the so-called pure vibrational vdW shift, the triple correlation, which has been found between the coupling strength, the amplitude of the vdW wavefunction in the bending coordinate, and the relaxation rate, is a feature of remarkable beauty.

Further investigation of the internal vibrational dynamics of this interesting vdW system by appropriate quantum multidimensional theoretical approaches is needed to confirm the conclusions which have been asserted on a mostly experimental basis.

### ACKNOWLEDGMENTS

We wish to thank D. Pratt for sending us the preprint of his work on the aniline–Ar vdW complex. We are grateful also to P. Parneix, D. Consalvo, and H. Dreizler for useful discussions. Support from the EC (under Contract No. TM-RERBFMGECT950017) and Italian MURST are gratefully acknowledged. One of us (N.M.L.) wishes to thank the EC for the fellowship ERBFMBICT961046.

## APPENDIX: CONSTRUCTION OF SYNTHETIC SPECTRA AND FRANCK-CONDON FACTORS

We present here some details of the intermediate procedures which were used to recover the branching ratios for the initially excited complex state and the various VP-populated monomer final states by reconstruction of a synthetic spectrum and its comparison with the experimental spectrum.

First it should be noted that relation (2) can be fully justified from a rate equations analysis under the assumptions that the excitation laser pulse is rectangular in shape, and that the time integrated fluorescence is measured (this was achieved thanks to the boxcar integrator). Second the relationship between the fluorescence intensity  $I_{nm}$ , measured for a given band  $|n\rangle \rightarrow |m\rangle$ , and the population of the upper state responsible for this band involves both experimental factors, such as the efficiency of collection, the transmission of the optical arrangement (lenses and monochromator), the overall gain of the detection system, and physical factors like the partial spontaneous emission rate constant characteristic of the transition, the fluorescence quantum yield, and the purely radiative lifetime of the upper state. Considering that the spectral region which was actually used is rather narrow, it is a good approximation to assume that all the experimental factors are spectrally independent. The partial spontaneous emission rate is proportional to the Franck– Condon factor of the transition, and its spectral dependence can be neglected over the narrow region. Since we have seen that the lifetimes of the upper states are all the same, it implies that the fluorescence quantum yield and the radiative lifetime are state independent. Thus, finally, the timeintegrated fluorescence intensity of a given band appears simply as proportional (with always the same proportionality constant, C) to the Franck–Condon factor of the band under measurement, and of course to the population of the upper state:

$$I_{nm} = CN_n \langle n | m \rangle^2$$
.

Only the relative Franck-Condon factors are needed. The set that we used is given in Table VII, in which  $\langle 00 \rangle^2 = 1$  is taken as reference. The first line corresponds to the  $0^0$  upper state. The numbers are averaged over data in Refs. 27-29. The third, fourth, and fifth lines corresponds to the  $6a^1$ ,  $I^2$ , and 1<sup>1</sup> upper states, respectively. The numbers were obtained by remeasuring the corresponding transitions with our setup. These lines were scaled with respect to each other using the data in Ref. 30 (LIF excitation spectrum) and Ref. 31 (photoacoustic absorption spectrum). The second line corresponds to the  $I^1$  upper state. The numbers have been obtained from Ref. 27, and scaled relative to  $\langle 0|0\rangle^2$  using the data in Refs. 32 and 33. For all the states which usually appear in sequence bands, like  $10b_1^1$ ,  $16a_1^1$ ,  $S_1^1$ , and so on, we have assumed that they give rise to progressions in emission with the same relative Franck–Condon factors as the  $0_0^0$ band. The  $N_n$  are the weighting factors which are used to build up the synthetic stick spectrum.

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