Vibrational predissociation dynamics of the aniline–neon van der Waals complex: an ab initio study

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Abstract

The aniline–neon van der Waals complex has been investigated from a theoretical point of view. The intermolecular distance, structure and rotational constants in the ground electronic state have been obtained by ab initio calculations using second-order Møller–Plesset (MP2) theory. The potential energy surface has also been determined. It has been found that two conformers exist: the *anti*, where the neon atom and the NH bonds are located on opposite sides of the ring, is slightly more stable than the *syn* conformer. All the ab initio results agree with those obtained by the analysis of the rotational and laser induced fluorescence spectra of this complex. We have also modeled the interaction of the van der Waals bending mode with others internal motions of the aniline molecule such as the inversion mode of the amino group and the breathing mode of the ring. The theoretical results predict that there is a significant coupling between the van der Waals bending and the inversion mode in agreement with the experimental behavior found in both the ground and the first excited electronic states of this complex.
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1. Introduction

Van der Waals complexes between an organic molecule and other small molecules (water, ammonia, diatomics, etc.) or atoms (rare gas) have been extensively used to elucidate the dynamics of photochemical and photophysical processes such as vibrational predissociation (VP) and intramolecular vibrational redistribution (IVR) [1,2]. This is due to the fact that such complexes not only usually exhibit binding energies much lower than some cromophore vibrational frequencies but also have large amplitude anharmonic motions that make possible a coupling between the intermolecular and the intramolecular vibrational states. Moreover, these systems are also of great interest to study the shape of the intermolecular potential energy surface since these can be described by a superposition of a number of dominant interaction energy terms [3,4].

The use of modern high resolution spectroscopy and molecular beam techniques allows for obtaining information on structure, energy levels, internal motion, dynamics and redistribution of energy in such weakly bound systems [5]. The van der Waals complex of the aniline molecule with a single rare gas atom has attracted much attention [2,6–10] and this work is focused on the study of the aniline–Ne complex. In previous work [9–11] we have recorded the high resolution excitation spectra of three vibronic bands, $6a_0^1$, I_0^2 and 1_0^1, of the S_1–S_0 transition. The rotational contours of these spectra were analyzed yielding information on rotational constants, band origin frequencies, molecular structure and linewidths of the transitions in both the ground and the first excited electronic states. Although we have obtained the effective coordinates for the neon atom from the experimental rotational constants in the S_0 state, we could not determine the relative position of the neon with respect to the amino hydrogens. The

amino group in the aniline molecule has a pyramidal structure and therefore, both sides of the aromatic plane become non-equivalent leading to two types of conformers for the aniline–Ne complex. The neon atom positioned on the opposite side of the ring with respect to the NH amino bonds corresponds to the *anti* conformer while in the *syn* conformer the neon atom is on the same side of the ring where the NH bonds are located.

Moreover, we were able to extract information about the vibrational dynamics occurring in its S_1 excited state by combining the laser-induced fluorescence excitation spectra (high resolution) and the dispersed emission [2,11]. We concluded that the excitation of the inversion motion, if compared to that of in-plane vibrations, is followed by a very fast dynamics. Also in the S_0 state some authors [12] have observed a fast relaxation decay for the I^2 vibrational state of the aniline–Ne complex. The interplay between the direct VP and IVR is rather complicated in this system and we provided different evidences for contemporary presence of both relaxation processes for the S_1 excited states. IVR seems to play a major role when occasional resonances occur or a large linewidth is observed, as the density of accepting states for relaxation (coupled by third or fourth order anharmonic terms to the initially prepared level) is rather sparse [11].

In this paper, we investigate the aniline–Ne complex from a theoretical point of view in order to shed light on the equilibrium structure of this complex and to estimate its binding energy from ab initio calculations. To this purpose we have investigated the potential energy surface of both conformers of the complex. This enables us not only to check its equilibrium structure but also to understand the neon–nitrogen interaction which mainly governs the stability of these conformers as was shown for the aniline–Ar complex [13]. The theoretical results are compared to the existing experimental data. Furthermore, we have modeled the interaction of the van der Waals bending with the inversion mode of amino group and with the breathing mode of aniline in order to predict the experimental behaviour about the coupling of intra and intermolecular vibrations in the aniline–Ne complex giving a vibrational predissociation phenomenon. Finally, by comparing the theoretical results with the experimental ones we will be able to verify the accuracy of ab initio calculations in order to estimate the properties of different van der Waals complexes.

2. Ab initio calculations

The optimized equilibrium structure and the interaction energy of the aniline–Ne complex have been calculated by second-order Møller–Plesset perturbation theory (MP2 method), with the cc-pvdz and aug-cc-pvtz basis set for the aniline and for the Ne atom, respectively. To compute accurately very small energy differences in van der Waals complexes is difficult, since the interaction energy depends on the level of calculation as occurred in the benzene–argon complex [14]. In spite of that it has been demonstrated that the MP2 method provides reliable results in agreement with the experimental data [15]. It has also been shown that the stabilization energy at the MP2 level is almost identical to that calculated at the MP4 level: for the benzene–helium they differ by less than 1% [16]. Furthermore, in previous work [13] we have analyzed the aniline–Ar complex with the above mentioned level of calculation yielding values for the intermolecular distance, rotational constants and binding energy in agreement with the experimental results. Therefore, we have chosen this level of theory as a starting point for the study of aniline–Ne complex. We have also used the aug-cc-pvdz basis set for the aniline molecule in order to check the effect of the basis set size on the results. The basis set superposition error (BSSE) has been corrected by using the counterpoise method of Boys and Bernardi [17] and all of calculations have been carried out by using the GAUSSIAN 98 [18] program.

3. Results and discussion

### 3.1. Equilibrium structure of aniline–Ne complex

The structure has been optimized according to a C_s point of group in which the symmetry plane is perpendicular to the aromatic ring and contains the neon atom and the CN bond of aniline. Table 1 shows the experimental and calculated structure of the isolated aniline and of the aniline–Ne complex. Fig. 1 shows the labelled atoms and two relevant parameters of the amino group; the inversion angle (ϕ) defined as the angle between the ring and the NH_2 planes and the γ angle defined between the ring plane and the CN bond. It can be seen that the aromatic ring of the aniline molecule is almost planar. The nitrogen atom lies out of the ring plane by $\gamma = +3°$, while the amino group has an inversion angle of $+47°$ resulting in a pyramidal structure. This optimized geometry agrees with the experimental data obtained from the analysis of the microwave (MW) spectrum [19,20]. It can be also noted that the aniline structure does not change when the complex is formed. Therefore, the aniline structure was kept fixed in all calculations.

The MP2 binding energy difference between the optimized structures of both conformers without BSSE correction is about 16 cm^{-1}, being more stable the *syn* conformer than the *anti* one. To find the equilibrium structure of the complex we have calculated the MP2 BSSE corrected potential energy surface (PES) as a function of the Ne position along the three principal

Table 1

Experimental and calculated geometry of aniline in the ground state for the isolated molecule and for the two conformers of aniline–Ne complex

	Experimental[a]	Calculated		
	Aniline	Aniline[c]	*syn* Aniline–Ne[d]	*anti* Aniline–Ne[d]
Distances (Å)				
N–H	1.001	1.019	1.019	1.019
C_1–N	1.402	1.411	1.410	1.410
C_1–C_2	1.397	1.411	1.411	1.411
C_2–C_3	1.394	1.403	1.403	1.403
C_3–C_4	1.396	1.405	1.405	1.405
C_2–H_2	1.082	1.096	1.097	1.097
C_3–H_3	1.083	1.095	1.095	1.095
C_4–H_4	1.080	1.094	1.094	1.094
Angles (°)				
HNH	113.1	108.5	108.4	108.5
$C_6C_1C_2$	119.4	118.6	118.5	118.5
$C_3C_4C_5$	118.9	119.1	120.7	120.7
$C_1C_2C_3$	120.1	120.6	120.5	120.5
$C_2C_3C_4$	120.7	120.5	120.5	120.5
$H_2C_2C_3$	120.1	120.0	120.0	120.0
$H_3C_3C_2$	119.4	119.3	119.3	119.3
ϕ	43[b]	47	−47.2	46.7
γ	0.6	3	−3.2	3.6

[a] Ref. [19].
[b] Ref. [20].
[c] MP2/cc-pvdz values.
[d] MP2/cc-pvdz/aug-cc-pvtz values.
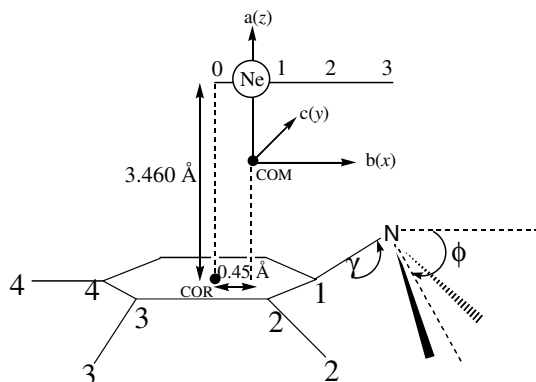
Fig. 1. Schematic representation of the *anti* aniline–Ne complex showing the reference frame, the label of the atoms, the angles regarding amino group and the positions of the Ne atom along the *x*-axis.

inertia axes of each complex, which have been taken as the reference frame. Fig. 1 also shows the principal inertia axes of the *anti* conformer and the corresponding Cartesian reference frame. The center of mass (COM) of the optimized structure is displaced 0.45 Å from the center of the aromatic ring (COR) toward the nitrogen in the *anti* conformer whereas the COM in the *syn* conformer is positioned at 0.41 Å from the COR. The *y*-positions of the COM are zero for both conformers while the *z*-position of the COM in the *anti* conformer is slightly closer to the ring plane than in the case of the *syn* conformer by only 0.009 Å. Fig. 2 shows the evo-

lution of the PES along the *z*-axis for both conformers. The *z*-equilibrium distances for the *anti* and *syn* conformers were found at 2.950 and 2.975 Å, respectively. Taking into account that the aromatic plane is displaced by $z = -0.510$ Å from the COM of the respective complex and the *z*-displacement between the two COM is 0.009 Å, the distance between the Ne atom and the ring plane is $z = 3.460$ and $z = 3.494$ Å for the *anti* and *syn* conformers, respectively. These results agree with that obtained experimentally, 3.397 Å, from the analysis of the LIF spectrum [2,9] and moreover, they are very
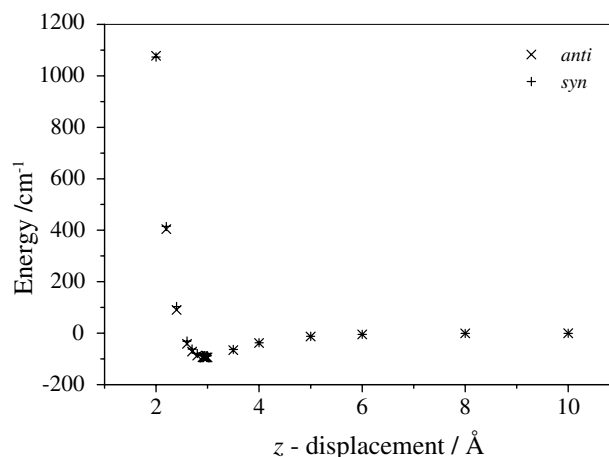
Fig. 2. Calculated PES as a function of the Ne position along the *z*-axis for both conformers of the aniline–Ne complex in the S_0 state. The displacements are referred to the COM of the *anti* conformer.

similar to those found in analogous aromatic complexes [21,22].

Furthermore, it can be seen in Fig. 2 that the equilibrium structure of the *anti* conformer is slightly more stable than the *syn* one. The calculated BSSE corrected binding energies for *anti* and *syn* conformers amount to 95.01 and 88.3 cm^{-1}, respectively, the experimental zero point energy amounting to ca. 31 cm^{-1} [11]. It means that the binding energy difference between the two conformers is only 7 cm^{-1}. This value is not only different from that obtained without BSSE correction but also the relative stability of the conformers is reversed. Although this result agrees with the experimental data obtained from the analysis of the MW spectrum of the ^{15}N-isotopomer [22], this energy difference is too small to be conclusive since tunnelling effects between the conformers could be not completely quenched as just occurred in the aniline–Ar complex [6].

Fig. 3 shows the evolution of the PES as a function of the Ne position along the *y*-axis for both conformers. Due to symmetry reasons, the *y*-equilibrium position of the Ne atom is zero. It can be seen that the *anti* conformer is slightly more stable than the *syn* one at shorter displacements.

The PES as a function of the Ne position along the *x*-axis is shown in Fig. 4. In this case, this function is asymmetric due to the interaction between the Ne atom and the amino group showing a similar behavior to that found in the aniline–Ar complex. For *x*-displacements smaller than 1.5 Å the *anti* conformer is slightly more stable than the *syn* one while the opposite occurs for displacements larger than 1.5 Å. At about $x = 2.5$ Å there is an energy difference between both conformers of 22 cm^{-1} being the *anti* conformer less stable than the *syn* one. This is due to the repulsion between the Ne atom and the lone pair of the nitrogen atom and this interaction is expected to be smaller than in the case of the
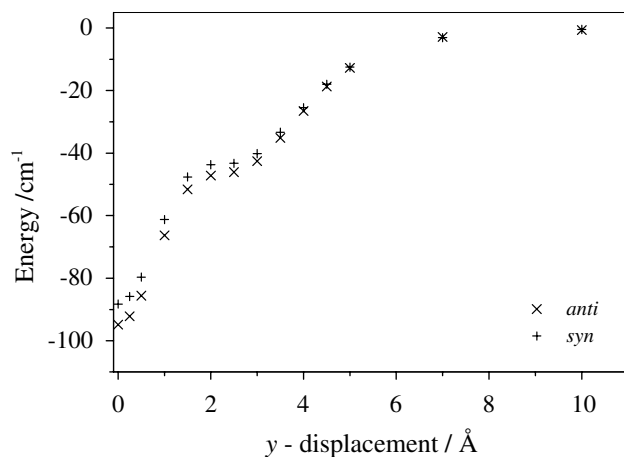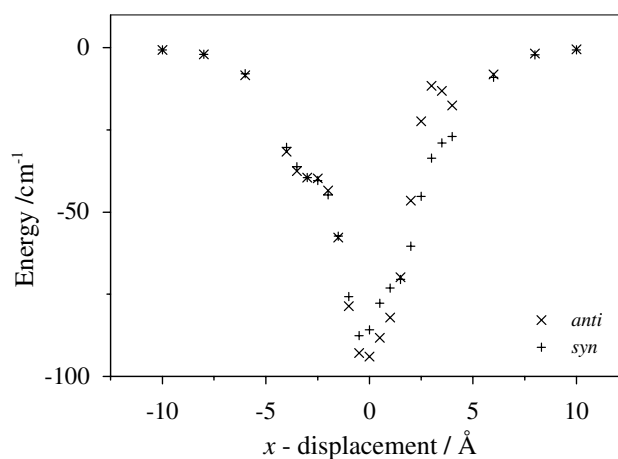

Fig. 4. Calculated PES as a function of the Ne position along the *x*-axis for both conformers of the aniline–Ne complex in the S_0 state.

aniline–Ar complex due to the different polarizability of the two attached rare gas atom. For instance, the energy difference between the conformers of the aniline–Ar complex [13] at $x = 2.5$ Å is twice than in the aniline–Ne system. The *x*-equilibrium position of the Ne atom is $x = -0.14$ and $x = -0.36$ Å from the COM of the respective complex for the *anti* and *syn* conformers, respectively. This means that the θ angle between the *z*-axis and the line connecting the origin and the Ne atom is 8° and 21° for *anti* and *syn* conformers, respectively. Therefore the Ne atom is displaced away from the COR toward the nitrogen in agreement with the experimental data obtained for this complex as well as for similar systems [9,21]. Moreover, the calculated intermolecular distance and the position of the Ne atom close to the nitrogen is shorter in aniline–Ne than in aniline–Ar, in agreement with the relative sizes of the rare gas atoms and with the experimental data.

Also, the calculated rotational constants for both conformers at the equilibrium structure agree with those obtained from the analysis of the LIF spectrum (Table 2) if the vibrational averaging of the Ne atom along the three axes is taken into account [9]. In fact, two-*anti* and two-*syn* orientations had been determined

Fig. 3. Calculated PES as a function of the Ne position along the *y*-axis for both conformers of the aniline–Ne complex in the S_0 state.

Table 2
Experimental rotational constants of aniline–Ne complex and calculated values derived from the equilibrium structure of the two conformers

	Experimental[a,b]	Calculated[c]	
		anti	*syn*
A (cm^{-1})	0.06181(3)	0.06024	0.06312
B (cm^{-1})	0.05744(20)	0.05682	0.05321
C (cm^{-1})	0.04378(20)	0.04270	0.04192

[a] Numbers in parenthesis represent the standard deviation of the parameter in units of the last quoted decimal place.
[b] Ref. [9].
[c] MP2/cc-pvdz/aug-cc-pvtz values.

compatible with the moments of inertia and it was necessary to analyze the rotational spectrum of the ^{15}N-isotopomer to deduce that the *anti* conformer is more stable than the *syn* one [22]. If we take a binding energy range of 10 cm^{-1} around the equilibrium position for both conformers, the displacements range of the Ne atom is ± 0.1 Å along the z-axis and ± 0.5 Å along the x- and y-axes. These values are slightly higher than in the case of aniline–Ar complex. All these results are in agreement with the experimental large amplitude motion of the Ne atom along the three axes which indicate than the motion of the Ne atom in a plane parallel to the ring is less hindered than in the perpendicular direction, showing larger values than for the Ar atom [9].

Following the same procedure, we have also calculated the equilibrium structure and the corrected BSSE binding energy for both conformers with the augmented aug-cc-pvdz and aug-cc-pvtz basis set for the aniline molecule and the Ne atom, respectively. In this case, the intermolecular distance for the *anti* and *syn* conformers is 3.361 Å and 3.389 Å, respectively. The x- and y-equilibrium positions for the Ne atom do not change with respect to the previous ones and the PES along these axes do not show qualitative differences with respect to those obtained with the smaller basis set. The PES as a function of the Ne atom along the x-axis for the *anti* conformer with the employed basis sets is represented in Fig. 5. The only difference between both curves is the depth of the minimum. In this case, the binding energy is 133 and 127 cm^{-1} for the *anti* and *syn* conformers, respectively. It means that the *anti* conformer is still more stable than the *syn* one by only 6 cm^{-1} as obtained previously. Therefore, the augmented basis set reproduces the previous behaviour for the conformers of the aniline–Ne complex, the only difference being the calculated interaction energy which, in this case, agrees with that obtained from semiempirical

PES (142 cm^{-1} [2]). This shows that it is necessary to use a larger basis set to reproduce the binding energy in complexes where the van der Waals interaction is weak.

3.2. Interaction of the van der Waals bending motion with the inversion mode of amino group

First, the inversion motion of the amino group for isolated aniline has been investigated. We have considered the planar structure with a C$_{2v}$ symmetry as a starting point and then, we have varied the inversion angle from $\phi = +60°$ to $\phi = -60°$. This range corresponds approximately to the amplitude of vibration in a molecule excited with two quanta of the inversion mode. Simultaneously, the γ angle has been also varied according to the N/H displacement ratio indicated in the calculated MP2/cc-pvdz eigenvector corresponding to this normal mode. In this way, we can reproduce the typical umbrella-like motion of the ammonia molecule. In Table 3 we collect the energy values of the inversion potential for the aniline molecule at different inversion angles. It can be seen that the equilibrium conformation corresponds to an inversion angle between 35° and 40° and that the energy barrier height lies at about 410 cm^{-1} above both minima. These results are in agreement with the experimental data (inversion angle: 37–46° and barrier height: 450–560 cm^{-1}) [23–25].

Following, the Ne atom has been positioned at the previously determined equilibrium position of the *anti* conformer, that is, in the symmetry plane perpendicular to the aromatic ring, at the intermolecular distance of $z = 3.361$ Å. The inversion potential curves have been calculated for different x-positions of the Ne atom. In this case, the COR has been taken as a reference frame. Therefore, the Ne atom is firstly positioned above the COR ($x = 0.0$) and then it is displaced to $x = +1.0, +2.0$ and $+3.0$ Å from this COR toward the nitrogen atom (see Fig. 1). We have chosen this interval of x-displacement because the amplitude of the van der Waals bending motion along this axes ranges up to 2.0 Å in the ground electronic state along both sides from the COR. In this way, we can evaluate the interaction between the amino inversion and the bending motion of the Ne atom up to $x = +3$ Å, where the Ne is above the nitrogen.

Table 3 collects the difference between the values of the inversion potential energy for the aniline–Ne complex and those of free aniline at selected x-positions. These energy values are also shown in Fig. 6. The negative values of the ϕ angle correspond to *anti* conformations, whereas the positive angles correspond to *syn* conformations. It can be seen that the inversion potential-well becomes asymmetric when the Ne atom is attached to the aromatic ring being the *anti* conformer more stable than the *syn* one at $x = 0.0$ and $+1.0$ Å, while the opposite occurs at $x = +2.0$ and $+3.0$ Å positions. The energy difference between the two minima of
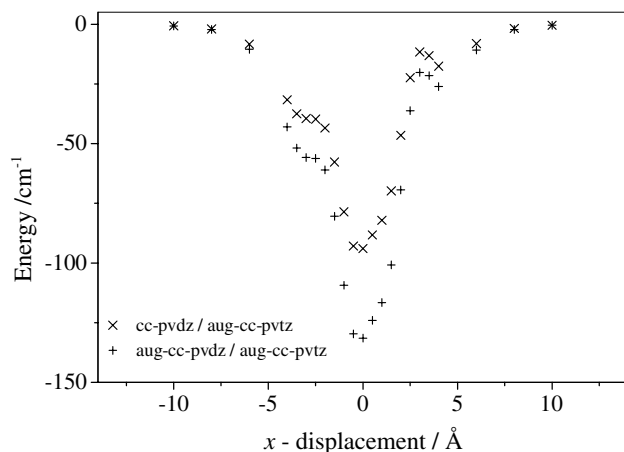

Fig. 5. Comparison between the PES calculated with cc-pvdz/aug-cc-pvtz and aug-ccpvdz/aug-cc-pvtz basis sets as a function of the Ne position along the x-axis for the *anti* aniline–Ne complex.

Table 3
Energies values (cm^{-1}) of the inversion potential for the aniline molecule at different inversion angles and their changes in the complex for the selected positions of the Ne atom along the x-axis

Inv. angle (ϕ)	Aniline	x-positions of the Ne atom[a] (Å)			
		0.0	+1.0	+2.0	+3.0
−60	835.784	−2.919	−5.971	−3.622	−0.615
−50	−28.079	−2.678	−5.400	−2.239	1.383
−40	−378.771	−2.371	−4.698	−1.163	2.744
−35	−410.648	−2.129	−4.259	−0.702	3.117
−30	−382.920	−1.909	−3.754	−0.307	3.336
−25	−315.631	−1.646	−3.271	−0.022	3.381
−20	−230.296	−1.361	−2.678	0.154	3.117
−10	−65.773	−0.702	−1.405	0.285	2.019
0	0.000	0.000	0.000	0.000	0.000
10	−65.773	0.702	1.405	−0.615	−2.678
20	−230.296	1.339	2.700	−1.493	−5.796
25	−315.631	1.668	3.315	−2.019	−7.464
30	−382.920	1.931	3.8119	−2.612	−9.155
35	−410.648	2.195	4.259	−3.271	−10.911
40	−378.771	2.415	4.654	−3.974	−12.689
50	−28.079	2.832	5.247	−5.488	−16.092
60	835.784	3.117	5.488	−7.069	−19.209

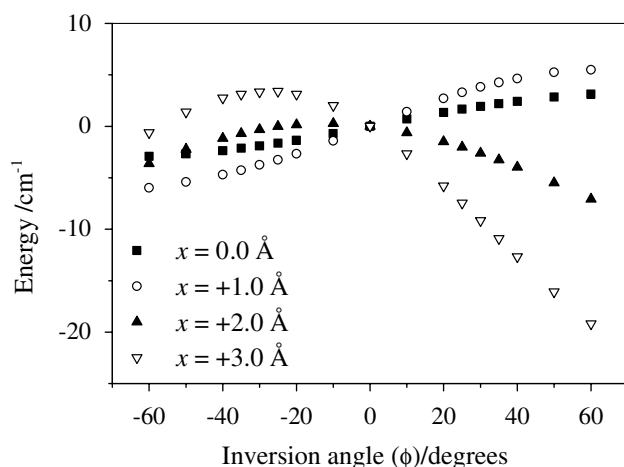[a] Relative to the x-position of the COR.

Fig. 6. Difference-potential energy curves between the inversion potential curve of the aniline molecule and of the aniline–Ne complex for different positions of the Ne atom moved out from the COR along the x-axis (0, 1, 2, 3 Å).

the inversion potential at $\phi = \pm35°$ (−4.3, −8.4, +2.4 and +14 cm^{-1} at $x = 0.0, +1.0, +2.0$ and $+3.0$ Å, respectively) is comparable to that found between the two equilibrium structures (7 cm^{-1}) of each conformers. Furthermore, the energy difference between the two conformers at $\phi = \pm60°$ is slightly larger (−6, −11, +4 and +19 cm^{-1} at $x = 0.0, +1.0, +2.0$ and $+3.0$ Å, respectively). Although these differences are small, they represent approximately 5% of the inversion barrier height. Therefore, this result indicates that there is a small but significant coupling between the inversion and the van der Waals bending motions, in agreement with the experimental evidences obtained for aniline–Ne

complex by analysing the rotational structure of the I_0^2 vibronic band of the S_1–S_0 transition [2] and the lifetimes of the vibrationally excited aniline–Ne complex in S_0 state by performing pump-probe experiments [12]. It can be also concluded that the relative stability of the two conformers depends on the relative position of the Ne atom with respect to the amino group. Furthermore, the observed behaviour in the inversion potential curves at different positions of the Ne atom suggests an anisotropic interaction between the Ne atom and the nitrogen lone pair because of the electron density distribution of the nitrogen atom changes when the inversion motion occurs. Therefore, the interaction does not only depend on the distance between the atoms but also on the hybridization of the nitrogen [26].

3.3. Interaction of the van der Waals bending motion with the breathing mode of the ring

We have also studied the coupling of the motion of the Ne atom along the x-axis with the breathing mode of the aromatic ring. The distorted geometry along this last mode has been calculated according with the following equation:

$$\Delta q_i = Q_i L_i, \quad q = x, y, z,$$

where L_i is the eigenvector corresponding to mode i obtained from the calculated ab initio force field and Q_i is the classical turning point given by the expression [27]:

$$Q_i = [\hbar/\omega_i(2v_i + 1)]^{1/2},$$

where v_i is the vibrational quantum number and ω_i the corresponding wavenumber.

Thus, we have obtained three geometries of the aromatic ring which correspond to the positive breathing mode $(q_e + \Delta q)$, the equilibrium structure (q_e) and the negative breathing mode $(q_e - \Delta q)$, i.e., the undistorted and the extreme positions of the ring breathing amplitude. Therefore, we have calculated the interaction energy of the complex at the selected x-positions of the Ne $(x = 0.0, +1.0, +2.0$ and $+3.0$ Å) taking into account in each case the three geometries of the ring when the breathing mode occurs. Fig. 7 shows the effect of the Ne atom at several x-positions on the ring breathing mode of aniline. In each case the undistorted ring structure has been taken as a reference. The corresponding energy values are collected in Table 4. It can be seen that the interaction energy between the extreme breathing positions is much weaker than in the case of the inversion motion. For instance, the energy differences between the extreme breathing positions at $x = 0.0, +1.0, +2.0$ and $+3.0$ positions are 0.9, 2.1, 2.9 and 2.7 cm^{-1}, respectively, while those of the inversion motion at $\phi = \pm 60°$ are $-6, -11, +4$ and $+19$ cm^{-1}, respectively. This result indicates that the interaction between the bending van der Waals motion and the breathing mode is not sig-

nificant, in comparison to the coupling observed when the inversion is excited. This is in agreement with the experimental evidences [2,11,12]. This differentiated behavior of the coupling between the motion of the Ne atom with the inversion and breathing modes can be due to the fact that both, inversion and van der Waals bending, involve large amplitude motions which have low vibrational frequencies and large anharmonicities, while the breathing mode does not show these characteristics. The vibrational frequencies of the bending van der Waals mode of the aniline–Ne complex and the inversion motion of the isolated aniline are 22 and 41 cm^{-1} [8,23], respectively, while the breathing mode is measured at about 800 cm^{-1} [2]. This result is in agreement with the experimental behaviour observed in both ground and the first excited electronic state of the aniline–Ne complex [2,11,12], where it has been shown that the first overtone of the inversion motion (422 cm^{-1}) has shorter lifetime than other internal motions (6a and 1 modes).

4. Conclusions

We report, from ab initio calculations, on the pairwise interaction between the inversion (or ring-breathing) motion of aniline and the van der Waals bending mode in the aniline–Ne complex. These results, in comparison with the available experimental data, are rather useful for the evaluation of the relaxation process following vibrational (or vibronic) excitation. The inversion motion, very anharmonic, has a much larger interaction to the van der Waals modes than the (almost isoenergetic) in-plane, ring-breathing mode. This is possibly relevant for the interpretation of the relative role of the VP and IVR in the relaxation of these excited states. As we already discussed in [11], the density of accepting states for the first step in the IVR process (coupled by third or fourth order anharmonic terms to the initially prepared level) is rather sparse, in the order of 1–10 states per wavenumber. Given the observed linewidth for these vibronic bands, in the order of 1–5×10^{-3} cm^{-1}, it is quite difficult to have one accepting state for IVR relaxation within this bandwidth. Only in the case of the 12_0^1 band of aniline–^{22}Ne (an out of phase ring-breathing mode) an occasional resonance was detected, given the existence of a perturbation in the rotationally resolved spectrum [11]. In our opinion, the dominant relaxation mechanism for the in-plane vibronic bands is VP. Only when very large anharmonicity is present, as in the case of the I^2 level, the interaction terms are large enough to couple with states useful for initiating the IVR process. As we have reported here, the coupling of the intramolecular in-plane motions to van der Waals modes is much smaller. The number of states connected for the first steps of the IVR process is then
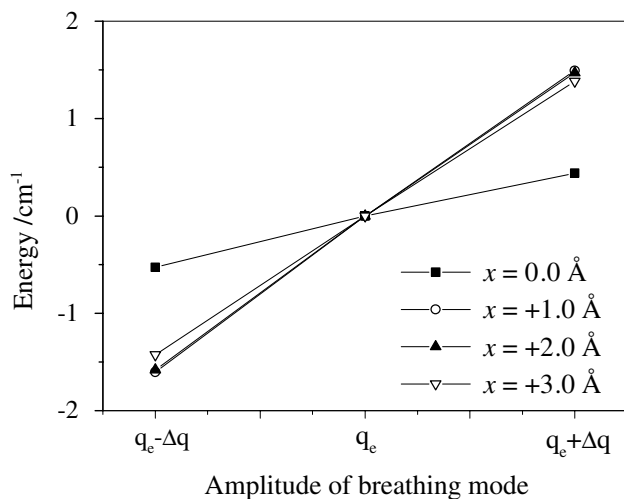

Fig. 7. Difference-potential energy curves between the potential curve of the ring breathing mode of the aniline molecule and of the aniline–Ne complex for different positions of the Ne atom moved out from the COR along the x-axis (0, 1, 2, 3 Å).

Table 4
Relative energy values (cm^{-1}) of aniline–Ne complex at different positions of both the breathing mode and the Ne atom along the x-axis

Breathing mode	x-positions of the Ne atom[a]			
	0.0 Å	+1.0 Å	+2.0 Å	+3.0 Å
$q_e + \Delta q$	0.439	1.493	1.471	1.3831
q_e	0.00	0.00	0.00	0.00
$q_e - \Delta q$	−0.527	−1.603	−1.581	−1.427

[a] Relative to the x-position of the COR.

much reduced: in most cases we have experimentally accessed it results to be equal to zero (only in the case of aniline–^{22}Ne we have observed the occasional resonance with one of those states). On the basis of present ab initio results and former experimental data, we can conclude that in the aniline–Ne complex the relaxation process occurs mostly through VP and IVR is possibly effective only in the case of excitation of the very anharmonic I^2 state (if no occasional resonances occur).

Acknowledgements

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