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Vibrational lifetimes of aniline–noble gas complexes

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Abstract

The lifetimes of electronic ground state, vibrationally excited aniline–noble gas complexes are measured in pump–probe experiments. When exciting the I_0^2-mode (422 cm^{-1}) of aniline–X (X = Ne, Ar), lifetimes are measured to be 36 ± 3 ns for the neon complex and 151 ± 34 ns for the argon complex. Upon deuteration of the amino group, the frequency of this mode shifts to 335 cm^{-1} and the lifetimes increase dramatically. Ring deuteration of aniline shortens the lifetime of the vibrationally excited aniline–argon complex to 29 ± 3 ns. Comparison of these results with statistical theory shows non-statistical behavior which is attributed to slow Internal Vibrational Redistribution (IVR). © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

To study and understand energy transfer at a fundamental level, weakly bound complexes, as for example noble gas atoms bound to simple molecules, can serve as model systems. In these systems, energy can be deposited in a controlled way into the degree of freedom of interest and the time evolution can then be monitored by laser probing schemes. Two processes are important: Internal Vibrational Redistribution (IVR) and Vibrational Predissociation (VP) [1]. The timescales of these processes vary with complex composition and internal excitation.

The dissociation of weakly bound complexes is also important in spectroscopic techniques, where the presence of a so called 'messenger particle' is used as a probe for the absorption of a photon [2]. These techniques rely on dissociation of the complex on a timescale which is shorter than the time-window for detection when making a transition to a level above the dissociation limit of the system.

Here, we present results on the dynamics of vibrationally excited aniline ($C_6H_5NH_2$) complexed with a noble gas atom. Several studies have been performed on the dissociation dynamics of electronically and vibrationally excited aniline noble gas atom complexes [3–7]. By using bright, tunable short pulse infrared (IR) lasers, such as the Free Electron Laser for Infrared eXperiments (FELIX) [8,9], the relaxation dynamics can also be studied for vibrationally excited complexes in the electronic ground state, which is a regime that is particularly relevant for modelling (thermal) energy transfer. In addition, it should be noted that experiments on the S_1 surface can not measure complex lifetimes that are longer than the radiative

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lifetime of the S_1 state. On the electronic ground state surface, however, the ultimate physical limit is given by the radiative lifetime of the vibrationally excited state, which is on the millisecond timescale. Realistically, an upper limit for the lifetimes that can be measured is given by the interaction time of the complexes with the lasers, which is on the order of a few microseconds when using molecular beam techniques.

In previous experiments, it has been observed that, in the region between 300 and 2000 cm^{-1}, one normal mode dominates the infrared spectrum of aniline [10]. This mode gives rise to two strong features in the IR spectrum in this range, corresponding to two levels in the inversion mode potential of the NH_2 group [11–14]. In the argon complexes, the I_0^2 transition occurs at a photon energy of 422 cm^{-1} for both aniline–h_2 and aniline–d_5, and at 335 cm^{-1} for aniline–d_2. These frequencies do not shift significantly when changing from the argon complex to the neon complex, and are only slightly above the dissociation limit D_0 of the complexes, bracketed between 273 and 329 cm^{-1} for the argon complex [10] and expected around 142 cm^{-1} for the neon complex [7].

2. Experiment

The pump–probe experiments are performed in a pulsed molecular beam machine equipped with a time-of-flight (TOF) mass spectrometer. A scheme of the setup is shown in Fig. 1. The setup consists of two differentially pumped vacuum chambers. The two chambers are separated by a skimmer with a circular opening of 1 mm. In the source chamber, a pulsed valve is mounted (R.M. Jordan Company). Through this valve, aniline vapor, seeded in the appropriate noble gas (argon or neon), is injected at a total stagnation pressure of 3 bar. The valve runs at a repetition rate of 10 Hz and the gas pulses have a duration of about 50 µs. In the expansion, cooling occurs through multiple collisions and complexes are formed. The expansion is skimmed 4 cm downstream, thus forming a molecular beam which enters the second chamber. The first laser (in time) to interact with the complexes is FELIX. The FELIX output consists of
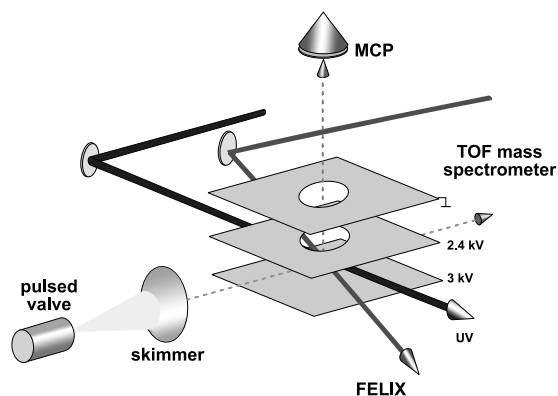

Fig. 1. A schematic overview of the experimental apparatus. The lasers intersect the molecular beam between the electrodes of the TOF assembly. The created ions are accelerated toward the MCP detector.

µs-long macropulses, which have a substructure of picosecond duration micropulses. The micropulse spacing in the macropulse is set to 40 ns. The macropulse repetition rate is set to 5 Hz. Tunability is continuous and covers the range between 40 and 2000 cm^{-1}, with a bandwidth of about 0.5% of the central frequency. The energy in one macropulse amounts to 2.5 mJ. FELIX is used to vibrationally excite the aniline–X (X = Ar, Ne) complexes. These complexes can undergo IVR and dissociation, when the excitation is above the dissociation threshold. The population of vibrationally excited complexes is monitored, as a function of time delay with respect to a micropulse, by performing 1+1 REMPI from this vibrationally excited level. The intermediate level to which we tune our probe laser, is the vibrationless excited singlet state S_1. For probing, the frequency doubled output of a dye laser (Spectra Physics PDL-2), pumped by a Nd:YAG laser (Continuum Surelite II), is used. A second UV laser photon ionizes the aniline–X complex, with about 5000 cm^{-1} excess energy [12,15]. The UV laser is synchronised to a micropulse of FELIX to better than one nanosecond. The attainable time resolution is determined only by the duration of the UV pulse, which is 3–4 ns. None of the lasers employed can select individual rotational levels of the complex. The measured lifetimes are thus averages over the rotational distribution in the molecular beam. The electrodes of the TOF assembly are

kept at a fixed potential. The lower electrode is at 3000 V, the second one is at 2430 V and the upper electrode, as well as the flight tube, is at ground potential. The positive ions created in the 1+1 REMPI process are thus accelerated into a 20 cm long flight tube, at the end of which a micro-channel plate (MCP) detector detects the ions. The signal from this detector is amplified and fed into a digital oscilloscope (LeCroy 9430).

3. Results and discussion

FELIX is tuned to the transition corresponding to the inversion mode of the NH_2 group in aniline at 422 cm^{-1} and irradiates the aniline–noble gas complexes. The vibrationally excited complexes are monitored using the 1+1 REMPI scheme described in Section 2. In Fig. 2, the ion intensity of the complex is shown as a function of the time delay between the UV laser and FELIX, both for aniline–Ar and aniline–Ne complexes. FELIX runs at a repetition rate of 25 MHz and maxima in signal intensity are observed when the UV laser coincides in time with a FELIX micropulse. In the figure, a time window of 80 ns is shown and the overlap with two FELIX micropulses (arrows), spaced 40 ns apart, is clearly observed. In between the two pulses the signal decays because of IVR and/or dissociation of the vibrationally excited complexes. The observed time structure is a convolution of the FELIX micropulse structure, the pulse widths of the two lasers and an exponential decay of the vibrationally excited complex. The smooth curves shown in the figure represent fits of such convolutions with, as adjustable parameters, the lifetimes of the excited complexes. The extracted lifetimes for the aniline–h_2–noble gas complexes excited at 422 cm^{-1} are 36 ± 3 and 151 ± 34 ns for the neon and argon complexes, respectively. In the same figure two traces are shown that are obtained when using deuterated species of aniline. For aniline–d_5–argon (all ring positions deuterated) we find a lifetime of 29 ± 3 ns. By deuterating the ring, the frequencies of the ring vibrations are lowered. Little change is observed in the I_0^2 transition frequency, however. When, on the other hand, deuterating only the
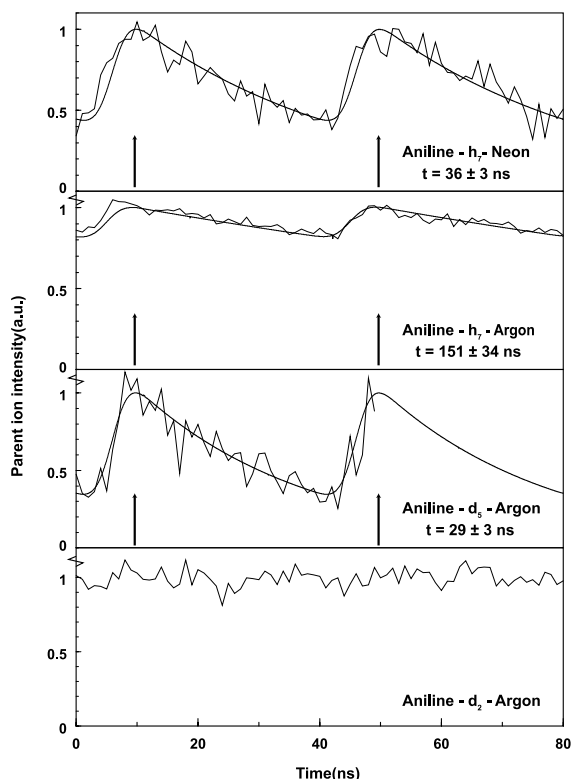

Fig. 2. By varying the delay time between an infrared micropulse and the UV pulse, transients are obtained for the various aniline–X (X = Ar, Ne) species. The smooth curves are exponentially decaying fits to these transients; the $1/e$ decay times are given in the figure. The times at which there is temporal overlap of the laser pulses is indicated by arrows.

amino group, there is little change in the frequency of the ring vibrations, whereas there is a significant change in transition energy for the I_0^2 mode, which is then at 335 cm^{-1}. The bottom trace in Fig. 2 shows the result that is obtained for aniline–d_2–argon, for which the excitation energy is only slightly above the dissociation threshold. This trace shows no recognizable time structure, indicating that this complex has a lifetime exceeding several hundreds of nanoseconds. Not shown here is the trace that is obtained for the aniline–d_2–neon complex, which also has a lifetime of this order. Lifetimes of several hundreds of nanoseconds are difficult to measure using the present setup as it is difficult to abruptly turn off FELIX and as the complexes in the beam leave the interaction region with the lasers on a microsecond timescale. As a

lower limit, lifetimes of at least several hundreds of nanoseconds are inferred from the measurements reported here and it might be that the complexes have a very long lifetime or do not undergo IVR and dissociation at all.

If the complexes would behave statistically, i.e., very fast energy flow and randomization of energy in phase space, the dissociation lifetime could be estimated using the well known RRKM theory [16]. As input, the vibrational frequencies are needed, which are calculated at the B3LYP/D95(d,p) level [17]. The transition frequencies corresponding to the NH_2 inversion mode are not described well when calculating the frequencies using the harmonic approximation. On the other hand, accurate experimental data on transitions involving this specific normal mode exist, and the experimentally determined frequencies at 41 cm^{-1} and at 422 cm^{-1} are used [18]. The frequencies of the intermolecular Van der Waals modes are taken from calculations by Parneix et al. [19]. We choose the stretching mode to be the coordinate of dissociation in the RRKM calculation. As the vibrational progression in the inversion mode is everything but harmonic, vibrational state densities are calculated on top of the ground state, the 41 cm^{-1}, and the 422 cm^{-1} mode. These are added up to obtain the density of states of the complex with which one can obtain the rate. The dissociation threshold is set to 300 cm^{-1} for aniline–h_2–argon and to 140 cm^{-1} for aniline–h_2–neon. In Fig. 3, we show the result of the RRKM calculations for both complexes together with the experimental data points. Due to the sparseness of the energy levels, the rates show strong oscillations with energy. The calculations show a much higher (more than four orders of magnitude) rate than experimentally observed, implying that, at the excitation levels used, the statistical picture does not apply. In the electronically excited S_1 state, the aniline–Ar complex is known to have significantly longer lifetimes for direct dissociation than predicted by RRKM theory as well [3–7]. From dispersed fluorescence studies it is also clear that the complex exhibits IVR [4–7].

In the experiments presented here, the disappearance of the population in the initially excited level is monitored. This population decrease can be
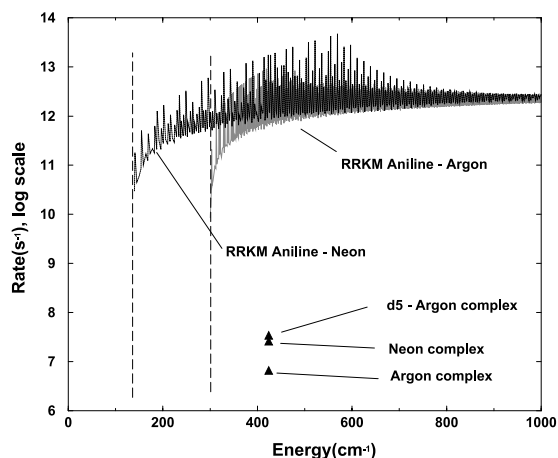

Fig. 3. Logarithmic plot of the results of the RRKM calculations for the dissociation rates of the two aniline–h_2 complexes, together with the observed decay rates of the vibrationally excited levels.

caused by IVR and/or complex dissociation. In order for the complex to undergo IVR or to dissociate, energy has to be transferred from the intramolecular degrees of freedom to the Van der Waals (VdW) bond. In principle, the complex could dissociate directly from the initially prepared level, by transferring all its vibrational energy into the VdW bond. Alternatively, the energy can be transferred step by step, i.e., the chromophore releases its energy quantum state by quantum state, and the energy in the VdW bond increases slowly. The first case would correspond to a direct VP while the second case corresponds to IVR followed by VP [1]. Wavefunction overlap arguments (the 'energy gap' rule [20]) suggest that the probability for energy exchange between quantum states decreases exponentially with the amount of energy that has to be exchanged. For the energy to be transferred at once from the aniline mode to the VdW mode, a few quanta of aniline intramolecular vibration have to be exchanged with many quanta of VdW vibration. It thus seems more likely that the system chooses to exchange the energy in several steps, thereby minimizing the exchange of energy (or quanta) in each step [21]. A pictorial representation of the IVR and dissociation process is given in Fig. 4. The intramolecular energy levels in aniline, as used in the density of states calculation, are shown, and on top
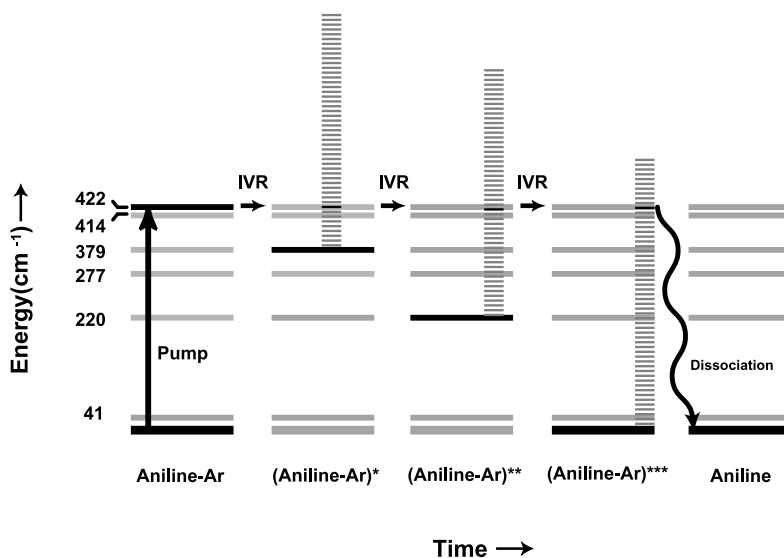
Fig. 4. Pictorial presentation of the process of IVR leading to the dissociation of the aniline–h_2–argon complex. Stepwise release of vibrational energy of the chromophore to the Van der Waals modes takes place, ultimately leading to dissociation.

of some of them, the energy level structure resulting from the VdW modes. Initially, FELIX excites the 422 cm^{-1} mode. From left to right, the energy in the aniline decreases while the energy in the VdW modes increases. An aniline mode that is only a few wavenumbers away (the 414 cm^{-1} mode, C–H in-plane bend) can most likely not be populated, as there are no corresponding states in the VdW vibrational subspace. One step might be to populate the 379 cm^{-1} mode (C–C bend) and transfer 43 cm^{-1} into the VdW modes. Whether that is likely or not depends on coupling between the initial state and these possible decay channels. At one point, enough energy will have accumulated in the VdW modes, and the complex can dissociate. In the case of neon, that is already the case when reaching the 220 cm^{-1} mode (C–C bend) in aniline while for argon, the system has to reach one of the two lowest states in order to dissociate.

When deuterating the aromatic ring of aniline, changes are made to the vibrational frequencies of the molecule. In the C–H stretch region, these changes are significant, whereas the changes in frequencies of C–H bend and C–C vibrations are less pronounced. Calculations on aniline–d_5 show that four low energy modes beneath 422 cm^{-1} shift somewhat in position with respect to aniline–h_7.

These subtle differences nevertheless have the effect of a five fold reduction of lifetime with respect to aniline–h_7–argon, demonstrating that wavefunction overlap at the initial level of excitation governs the rate of IVR and therefore the rate of dissociation. For deuterated aniline–d_2–noble gas complexes the excitation energy is lower, 335 cm^{-1}, whereas there is little change to the frequencies of the ring modes. The aniline–d_2–neon complex is expected to be about 200 cm^{-1}, and the argon complex at least 6 cm^{-1} above the dissociation limit. Yet, IVR (and likely dissociation as well) is observed to be very slow for both of them, if occurring at all. It might be the case that the direct coupling of the excitation to the VdW modes is very weak and that, due to the sparseness of the energy levels, a stepwise exchange is unfavorable as well. A detailed understanding of the microscopic processes involved has to involve more elaborate quantum mechanical modeling [22].

4. Conclusion

The lifetimes of electronic ground state, vibrationally excited aniline–noble gas complexes are measured by performing pump–probe experiments.

When excited to the NH_2 inversion mode at 422 cm^{-1}, we find that aniline–h$_2$–Ar has a lifetime of 151 ± 34 ns, for its neon counterpart we find a lifetime of 36 ± 3 ns. The importance of overlap with other states at the level of initial excitation is illustrated by the much shorter lifetime of aniline–d$_5$–argon; the factor five shorter lifetime of this complex upon ring deuteration is the direct result of slight shifts of vibrational levels of the aniline chromophore taking part in the IVR process. When deuterating the NH_2 group, the excitation frequency becomes 335 cm^{-1}, leading to a dramatic lengthening of the lifetimes.

For both, deuterated and non-deuterated aniline, the measured lifetimes can not be explained by statistical theories describing dissociation. It is likely that IVR is the rate limiting step in the dissociation process of the complex.

Acknowledgements

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