

Infrared spectroscopy of mass-selected neutral molecular systems without chromophore: the formamide monomer and dimer

B. LUCAS, G. GRÉGOIRE, F. LECOMTE, B. REIMANN, J. P. SCHERMANN and C. DESFRANÇOIS*

Laboratoire de Physique des Lasers, UMR 7538 CNRS-Université Paris-Nord, Institut Galilée,
Ave J.B. Clément, Villetaneuse 93430, France

(Received 30 November 2004; accepted 7 January 2005)

The paper presents IR spectroscopic data and theoretical frequency calculations, in the C–H and N–H stretch region, on jet-cooled formamide molecules and dimers. By using dipole-bound or quadrupole-bound anion formation, one is able to monitor IR absorption in the neutral beam on mass-selected species. For isolated formamide, resonant IR excitation leads to autodetachment of the excess electron in the dipole-bound anion. For the formamide dimer, the IR spectrum is characteristic from the cyclic dimer, with two neighbouring bonded N–H stretches and a complex spectrum with several lines and a broad absorption band in the C–H region absorption, as for the cyclic formic acid dimer. In this double H-bond configuration, IR absorption cannot lead to vibrational predissociation but it probably produces hot neutral dimers with large-amplitude intermolecular motions that reinforce autodetachment of the nascent weakly bound anions. Thus, the present original IR spectroscopic technique, which allows for rigorous mass-selection of the neutrals, seems to be relevant for any polar neutral species.

1. Introduction

The combination of infrared (IR) and ultraviolet (UV) spectroscopy with mass spectrometry (MS) of molecular species is a very powerful tool for the investigation of molecular conformations of neutral isolated molecules or molecular clusters [1, 2]. However, this method, using resonant two-photon ionization in the UV domain, requires the existence of a chromophore in the species of interest and this limitation applies for many families of molecules. For example, among the most common 20 natural amino acids, only three of them satisfy this condition. Fragmentation processes resulting from ionization should also be avoided as much as possible, so that mass spectrometry really reflects neutral mass selection. Recently, we have developed a new approach [3] that is not universal but satisfies the two preceding requirements. It is applicable to neutral molecular species which possess total dipole or quadrupole moments large enough to capture very low energy electrons. By means of Rydberg electron transfer (RET), stable dipole-bound or quadrupole-bound anions (DBA or QBA) are produced in which the excess electron is very weakly bound and located outside the neutral molecular frames in a very diffuse orbital [4]. As a

consequence, the neutral systems studied are ionized, thus allowing for mass discrimination, but the produced anions retain the geometrical configuration of their neutral parents and their fragmentation is totally negligible. Moreover, the RET process is resonant with respect to the excess electron binding energy (EBE) that critically depends on the total multipole (dipole, quadrupole, polarizability) moments of the neutral species, and thus to its geometrical configuration [5]. The ionization process itself is thus also structure-selective.

The principle of the experimental procedure is the following. Rydberg electrons are selectively transferred to a molecule or to a molecular complex in a given configuration leading to an anion signal which is recorded at the corresponding mass. Upstream this electron transfer region, the neutral molecular species are vibrationally excited by means of a tuneable IR laser. Rydberg electrons are thus transferred to species possessing an excess internal energy and that strongly influences the electron capture process. The IR excitation is thus monitored through the depletion of the anion signal, as in IR–UV–MS experiments in which a depletion of the cation signal is similarly induced by the IR resonant ‘burning’ of the vibrational ground state [6].

In the present experiments, the fate of the vibrationally-excited anions is dependent upon several different parameters. In our previous studies [3], polar neutral

* Corresponding author. Email: desfranc@lpl.univ-paris13.fr

dimers (water and formamide–water dimers) were vibrationally excited by means of IR photons with energies larger than the dimer intermolecular binding energies, thus leading to vibrational predissociation. For example, the dissociation energy of the formamide–water complex is lower than 300 meV [7], while photons with energies larger than 350 meV were used. In the present study, we consider IR excitation of isolated formamide molecules or formamide dimers. In the former case, the predissociation channel does not exist and in the latter case, the dissociation energy of the double H-bond complex is larger than IR photon energies. However, resonant anion depletions are still observed. After a short description of the experimental conditions and the calculations performed, we discuss the mechanisms responsible for these observations and the IR spectra obtained, as compared to previous experimental data and present quantum chemistry calculation results.

2. Experiment and calculations

The experimental procedure used here has already been described in some detail elsewhere [3]. A beam of laser-excited Rydberg atoms crosses at right angle a neutral beam of either formamide monomers or formamide complexes. This supersonic molecular beam is produced by means of a pulsed valve (General Valve, 0.15 mm conical nozzle) in which we flow few bars of helium that have passed over a heated reservoir (ca. 80°C) containing formamide. By tuning the time delay between the opening of the valve and the firing of the laser responsible for the excitation of the Rydberg atoms and subsequent RET ionization, we scan the pressure in the supersonic expansion and thus can favour either monomer or complex formation [7]. Electron transfer takes place in the collision region between the laser-excited atoms and the neutral molecular beam and monomer or dimer anions are produced, accelerated and detected at the end of a linear time-of-flight mass spectrometer. By tuning the wavelength of the laser responsible for the excitation of the Rydberg atoms and thus their principal quantum number n , we optimize either the monomer or the dimer anion formation rates, which are respectively peaked at $n = 13$ [7] and $n = 15$ [8]. Once either monomer or dimer anion signals are optimized, we cross the neutral molecular beam with the IR laser beam issued from a tuneable infrared OPO (optical parametric oscillator), upstream from the ionization region and a few hundred nanoseconds before the Rydberg excitation laser. As described in [3], this home-built OPO laser can be scanned between 2600 and 3900 cm^{-1} , its linewidth is about 1.5 cm^{-1} and the present energy per pulse between

1.5 and 2.5 mJ. Anion depletion signals are observed by performing real-time subtraction between anion signals obtained with and without the IR laser beam.

In order to interpret the present experimental data and to check the validity of the anharmonic frequency calculations, as recently implemented in the Gaussian03 software package [9], we also present calculation results obtained at the B3LYP/6-31++G(2d,2p) level of theory. Formamide or formamide dimer geometries are first fully optimized and further harmonic and anharmonic frequency calculations are performed. In all calculations, harmonic and anharmonic calculated frequencies are all real and the geometry of the formamide molecule is strictly planar. This was not the case in our previous calculations on formamide performed at the MP2 level, with the same basis set. In that case, the equilibrium geometry of the NH_2 group was found to be slightly pyramidal and we always obtained one imaginary frequency in the anharmonic calculations [3]. This may cause some artificial shift of the N–H stretch calculated values. In order to avoid this drawback and to deal with less demanding calculations, we shift to B3LYP calculations in the present work.

3 Results and discussion

3.1. Formamide monomer

Our aim here is to study the influence of a resonant IR excitation of the isolated formamide parent molecule with respect to the formamide DBA formation. In a collision between a Rydberg atom, with a principal quantum number n equal to 13, and a formamide molecule, a DBA can be produced in which the EBE is equal to 15 ± 2 meV [7]. This binding energy is considerably smaller than the IR photon energy, in the 320–480 meV range, thus allowing for vibrational autodetachment. If resonant IR absorption has occurred before ionization, the vibrationally excited neutral parent, $\text{M}(v = 1)$, gives rise to a vibrationally excited DBA, $\text{M}^-(v = 1)$, which is embedded into the continuum $\text{M}(v = 0) + e$. Any, even weak, energy exchange between the excess electron and vibrational motions, should lead to electron autodetachment. As displayed in figure 1, we indeed observe a depletion of the DBA signals for the IR photon energies corresponding to the excitation of the three modes in the scanned region: C–H stretch at 2857 cm^{-1} and symmetric and asymmetric N–H stretches at 3442 and 3558 cm^{-1} . As displayed in table 1, these frequency values are in very good agreement with previously reported high-resolution experimental data for isolated formamide in the gas phase [10] or in argon matrix [11]. However, it seems that our absolute values are systematically

overestimated by $3\text{--}4\text{ cm}^{-1}$ and this probably reflects some systematic shift in our calibration procedure. These results however demonstrate that autodetachment of nascent DBAs is efficient enough, like vibrational predissociation of neutral molecular complexes, to be used for detecting IR absorption and that the present spectroscopic method really holds also for isolated neutral molecules.

Let us consider the observed intensities of these three lines. As displayed in table 1, the calculated intensities of the N–H stretch modes (34 and 44 km/mol) are more than twice weaker than for the C–H stretch (96 km/mol). The experimental depletion signals are in the reverse order: 10% for the C–H stretch and 12–13% for the N–H stretch. The present discrepancy cannot be due to different laser energies since the measured energy per pulse was higher in the C–H region (2 mJ) than in the

asymmetric N–H region (1.6 mJ). On the contrary, in previous experiments on molecular complexes [3], the experimental line intensities were observed to qualitatively follow the calculated corresponding values. In that case, it seems that internal vibrational redistribution (IVR) is efficient enough to lead to vibrational predissociation of the complex, even when the excited mode is not directly involved in the intermolecular bond (free O–H or N–H modes). As a consequence, the observed anion depletion intensities, due to vibrational predissociation, really follow the IR absorption intensities of the neutral. In the present case of an isolated small molecule of formamide, the efficiency of dipole-bound anion autodetachment that is responsible for depletion seems to depend on the vibrational mode excited prior to ionization. This is quite surprising because this autodetachment process was expected to behave as photodetachment of dipole-bound anions, for which vibrational excitation has been observed to behaves as IR absorption of the neutral [12]. The above observations may thus suggest that IVR is not fully achieved within the time delay, of about $1\ \mu\text{s}$, between IR excitation and DBA production [13, 14]. We indeed propose the following explanation for the observed discrepancy in the line intensities. The dipole moment of formamide is roughly parallel to the C=O bond and the DBA excess electron is located on the positive side of this dipole moment, i.e. close to the two N–H bonds. The excess electron autodetachment process is due to a short-distance non-adiabatic coupling between the electronic and vibrational degrees of freedom. This coupling probably originates from the strong polarization forces that are exerted by the excess electron on the valence electron cloud, especially on the NH_2 side of the molecule. It is thus likely that energy exchange with the excess electron will be favoured for those modes that are on the positive side of the molecule, compared to modes that are far from the excess electron orbital. If this explanation is relevant, this effect should disappear in larger molecules, due to faster and more efficient IVR, and this should be

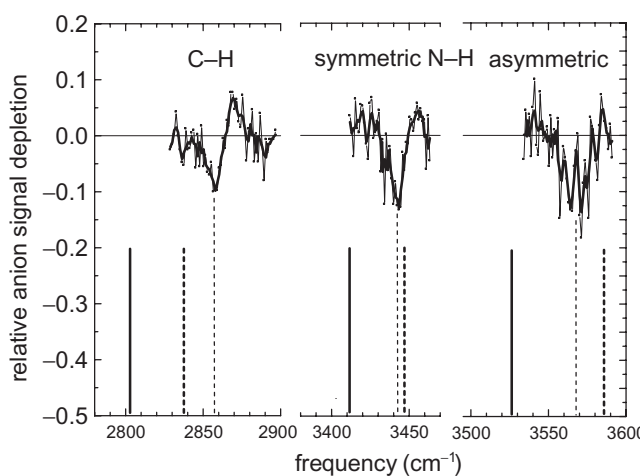


Figure 1. IR spectrum of jet-cooled formamide obtained from DBA signal depletion. Small squares correspond to relative depletion values averaged over four independent measurements, while full thick lines correspond to a smooth over three adjacent points. Experimental line positions are indicated by thin dashed lines and theoretical frequencies are located by full (anharmonic) and dashed (scaled harmonic) bars.

Table 1. Formamide theoretical and experimental frequencies (cm^{-1}). Theoretical values ν_h and ν_a are those of the present work obtained from B3LYP/6-31++G(2d,2p) harmonic or anharmonic (bold) calculations. Experimental values are those from gas-phase [10] and argon matrix [11] (in parenthesis) spectroscopy and from the present work (bold). $\Delta\nu$ is the difference between theoretical (scaled harmonic or anharmonic values) and experimental values.

Vibration	ν_h/ν_a	$\Delta\nu$	ν_{exp}	Scaling f	Average f	Intensity
Asym. N–H stretch	3734	+18	3564 (3555)	0.9555	0.9604	44
	3527	−42	3568			
Sym. N–H stretch	3589	+5	3439 (3430)	0.9590	0.9604	34
	3411	−32	3442			
C–H stretch	2955	−19	2854 (2876)	0.9668	0.9604	96
	2802	−56	2857			

experimentally checked in order to ascertain this interpretation.

We now discuss the shape of the observed spectrum. The depletion line corresponding to the C–H stretch absorption has a width of 10 cm^{-1} and it is followed by an increase of the anion signal on the high photon energy side, around 2870 cm^{-1} . We attribute this increase to the resonant predissociation of formamide–water complexes that were also present in the beam. The spectral dependency of this increase indeed coincides very well with that of the depletion signal corresponding to the C–H stretch excitation in the formamide–water complex at 2874 cm^{-1} [3]. Moreover, if we decrease the time delay between the opening of the pulsed valve, creating the molecular beam, and the firing of the Rydberg atom excitation laser, we probe the neutral molecular beam at a lower pressure and thus when the cluster production is lowered. We checked that, under these conditions, the depletion line is still observed at the same position while the increase at larger IR energies disappears. The same interpretation probably holds also for the less pronounced increase that can be also seen just after the symmetric N–H line since the position of this feature also coincides very well with that of the depletion observed for the bonded O–H stretch in formamide–water at 3454 cm^{-1} . The two N–H stretch depletion lines possess a similar width of about $16\text{--}17\text{ cm}^{-1}$ but the asymmetric mode displays a reproducible periodical structure which period is about 5 cm^{-1} . The formamide molecule is rather close to a symmetric top, with rotational constants $A = 2.43\text{ cm}^{-1}$ and $B \sim C \sim 0.35\text{ cm}^{-1}$, and a symmetry axis almost parallel to the N–O axis. The vibrational transition moments for the N–H stretches are thus approximately parallel, for the symmetric mode, and perpendicular, for the asymmetric mode, with respect to the symmetry axis. From the usual selection rules, the rotational spacing is expected to be much lower for the symmetric mode, i.e. of the order of $2B$, than for the asymmetric mode, i.e. of the order of $2(A-B)$. Although our resolution (1.5 cm^{-1}) is too low to obtain a quantitative agreement, it is likely that the structure observed on the asymmetric N–H line corresponds to the rotational contour at a low rotational temperature, as expected from the supersonic beam conditions.

The comparison between the calculated and observed vibrational frequencies of isolated formamide is given in table 1. For the three studied vibrational frequencies, the individual scaling factors, calculated as the ratio between present experimental and calculated harmonic frequencies, are consistent with one average value close to 0.96. This unique value will be used for the scaling of all dimer frequencies and leads to monomer scaled harmonic values that lie 20 cm^{-1} within the experimental

values. On the other hand, the absolute anharmonic values are always underestimated by 30 to 60 cm^{-1} . This relative lack of accuracy is quite surprising for such a simple molecule but the present B3LYP anharmonic results are at least as accurate as those previously obtained at the MP2 level [3].

3.2. Formamide dimer

The calculated lowest energy configuration of the neutral formamide complex is a head-to-tail cyclic configuration with a null total dipole moment but a rather large positive quadrupole moment, $Q = +48\text{ D}\text{\AA}$, that allows for the formation of stable quadrupole-bound anions (QBA), as studied in previous RET experiments [8, 15]. This double H-bond structure corresponds to a high dissociation energy, calculated to be $D_0 = 475\text{ meV}$, i.e. larger than the photon energies used in the present experiments that lie in between 350 and 450 meV (2800 to 3600 cm^{-1}). We found that this neutral complex also possesses two higher energy configurations, with a single H-bond, as displayed in figure 2. One configuration corresponds to a low dipole moment of 1.9 D , but still with a large positive quadrupole moment component on the dipole axis of about $+40\text{ D}\text{\AA}$, and to a lower dissociation energy

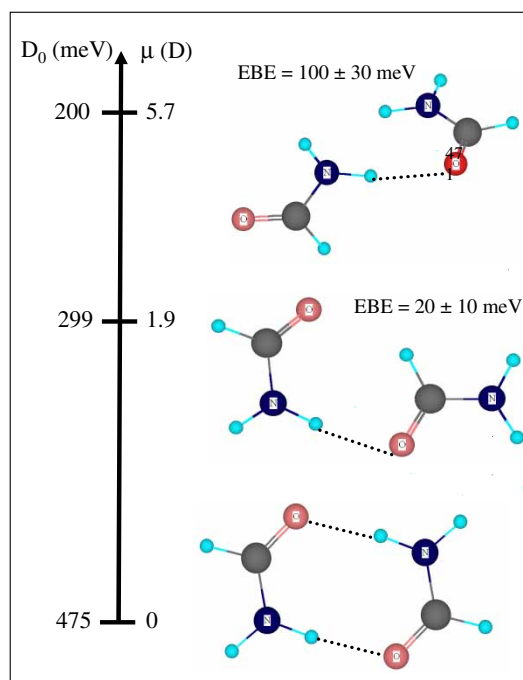


Figure 2. Calculated equilibrium structures of the formamide dimer. For each configuration, we give the calculated dissociation energy D_0 and total dipole moment μ (left axis). For the two higher energy structures, we also indicate the excess electron binding energy EBE for the corresponding DBA, as expected from model calculations.

$D_0 = 300$ meV. The last configuration lies at even higher energies ($D_0 = 200$ meV) and possesses a large dipole moment (5.9 D). These two formamide dimer structures should undergo vibrational predissociation upon IR absorption but they are unlikely to be populated in our supersonic neutral beam. Their energy difference with respect to the lowest cyclic configuration is indeed very large (175 or 275 meV) compared to the mean intermolecular energy of the dimers within the beam, which is surely lower than room temperature thermal energy (25 meV). Moreover, since experiments are performed at a Rydberg quantum number $n = 15$, the EBE of the observed anions must be about 10 meV [8]. In the case of the last configuration, the large dipole moment implies a much higher EBE value, i.e. about 100 meV from semi-empirical model calculations [16], and the corresponding DBA should be observed only at much lower Rydberg quantum number, i.e. $n = 6-7$ [5]. Thus, we will no longer consider this configuration. For the second configuration, the DBA EBE is expected to be also higher than 10 meV, i.e. about 20 meV from the same model calculations [16]. However, the uncertainty on this expected value leads us to still consider the possibility of the formation of such a dimer in our experimental conditions, even if most of the produced and detected dimers should be those of cyclic configuration.

The IR spectrum obtained for these formamide dimers is displayed in figure 3. It clearly exhibits several lines, in the free and bonded N–H and C–H stretch regions, with depletions up to more than 30%, i.e. much more intense than for the monomer. In this last region, i.e. from the lowest wavenumbers around 2750 cm^{-1} up to 3050 cm^{-1} , we observe a very broad background depletion of about 10–15%, on which many lines are

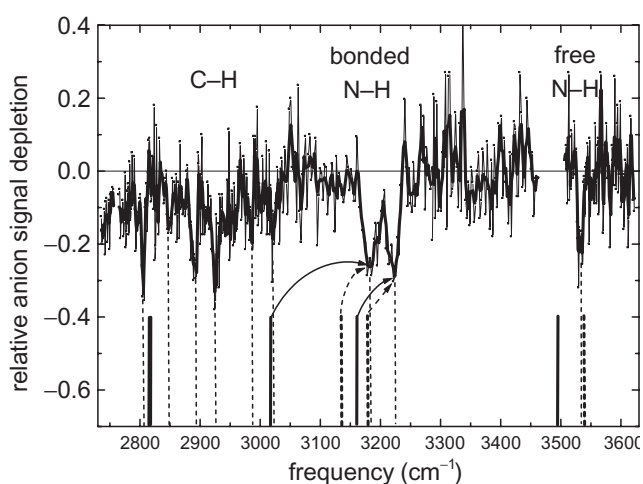


Figure 3. IR spectrum of mass-selected neutral formamide dimers, as in figure 1. Theoretical frequencies (full and dashed bars for anharmonic and scaled harmonic results) are those for the cyclic dimer structure.

superimposed. Three main peaks are located at 2805, 2893 and 2925 cm^{-1} , but three others less intense features can also be seen at 2848, 2987 and 3021 cm^{-1} . All these lines are rather narrow, with widths in between 6 and 14 cm^{-1} . The two intense lines observed in the bonded N–H stretch region, at 3183 and 3223 cm^{-1} , possess larger widths of about 30 cm^{-1} . The last, slightly less intense, line is located at 3532 cm^{-1} , in the free N–H stretch region, and its linewidth is about 12 cm^{-1} . All these frequency values are reported in table 2 together with previous experimental data obtained in Ar matrix [17] and assigned to the N–H stretch modes of the cyclic dimer. For the two highest N–H frequencies, the agreement is very good since our beam values are slightly higher (+17 and $+7\text{ cm}^{-1}$) than the Ar matrix values, as for the monomer (+13 and $+12\text{ cm}^{-1}$). For the lowest N–H frequency, our value (3183 cm^{-1}) is slightly lower than the matrix value (3195 cm^{-1}) but this unusual shift (-12 cm^{-1}) is also observed on the C–H mode of the monomer (-19 cm^{-1}) and can result for some matrix site effect. We note that all other lines observed in this matrix experiment, in between 3320 and 3370 cm^{-1} , do not appear on our spectrum and were assigned to some single H-bond open structure. This comparison strongly suggests that the present spectrum corresponds only to the cyclic dimer structure.

In order to try to interpret our IR spectrum, and to ascertain its assignment to the lowest energy cyclic conformer, we performed the same calculations as for the monomer. We thus computed harmonic and anharmonic frequencies of the two lowest energy configurations of the neutral formamide dimer, at the same level of theory as for the monomer. These are also displayed in table 2. First, we discuss the free N–H stretch frequencies whose calculated values, and particularly the scaled harmonic frequencies, are expected to be rather accurate, at least within a few tens of cm^{-1} . For the cyclic dimer configuration, we indeed obtain two almost degenerate scaled harmonic values at 3537 cm^{-1} , with a shift of -49 cm^{-1} with respect to the monomer, which are in very good agreement with the experimental values: 3532 and -36 cm^{-1} . For the second single H-bond configuration, one scaled harmonic frequency gives similar values, 3538 and -48 cm^{-1} , while the other one is noticeably higher and should have been observed close to the monomer asymmetric value (3568 cm^{-1}), with a comparable intensity. However, no clear line is observed in this region. The third free N–H frequency of this configuration is that of the free symmetric stretch and is also predicted to lie very close to the monomer frequency (3442 cm^{-1}), with a similar intensity. Again, no clear line is observed in this region.

We then examine the bonded N–H modes, for which both the anharmonic and the scaled harmonic values

Table 2. Formamide dimer theoretical and experimental frequencies (cm^{-1}). Theoretical values ν_h , ν_s and ν_a are those of the present work obtained from B3LYP/6-31++G(2d,2p) harmonic, scaled harmonic (with the scaling factor 0.9604 of table 1) or anharmonic (bold) calculations, for the lowest head-to-tail configuration (first line) and for the second possible configuration (second line). Experimental values are those from argon matrix [16] and from the present work (bold). $\Delta\nu$ are the frequency shifts with respect to the monomer.

Vibration	$\nu_h(\Delta\nu_h)$	$\nu_a(\Delta\nu_a)$	$\nu_{\text{exp}}(\Delta\nu_{\text{exp}})$	Scaled $\nu_h = \nu_s$	Intensity
Free N–H stretch	3683 (–51)	3496 (–31)	3515 (–40)	3537 (–49)	168
	3731 (–3)	3536 (+9)	3532 (–36)	3583 (–3)	51
	3682 (–52)	3496 (–31)		3536 (–50)	0
	3684 (–50)	3507 (–20)		3538 (–48)	80
Bonded N–H stretch	3312 (–277)	3160 (–251)	3216 (–214)	3181 (–266)	1337
	3587 (–2)	3417 (+6)	3223 (–219)	3445 (–2)	39
	3264 (–325)	3017 (–394)	3195 (–235)	3135 (–312)	0
	3337 (–252)	3180 (–231)	3183 (–259)	3205 (–242)	623
C–H stretch	2981 (+26)	2816 (+14)	3021/2987	2863 (+25)	0
	3018 (+63)	2866 (+64)	2925/2893	2898 (+60)	20
	2978 (+23)	2813 (+11)	2848/2805	2860 (+22)	278
	2952 (–3)	2792 (–10)		2835 (–3)	136

frequencies have been observed to be too much red-shifted with respect to the monomer, by $60\text{--}70\text{ cm}^{-1}$, in our previous work [3]. In the case of the cyclic dimer, the scaled harmonic calculations give 3181 and 3135 cm^{-1} while the anharmonic values are 3160 and 3017 cm^{-1} . Compared to the two experimental lines at 3223 and 3183 cm^{-1} , the scaled harmonic frequencies are indeed red-shifted by $40\text{--}50\text{ cm}^{-1}$ and their difference is in very good agreement with the experimental one, while the lowest anharmonic value is surprisingly much too low. The fact that the lowest frequency mode corresponds to a null calculated intensity results from the planar symmetry of the cyclic dimer equilibrium structure. In our experimental conditions, this symmetry rule is probably removed due to low-frequency out-of-plane modes ($60\text{--}200\text{ cm}^{-1}$) that are likely to be populated. For the second dimer configuration, the unique bonded N–H stretch value could be fitted only with the highest experimental frequency but would be red-shifted by only $20\text{--}40\text{ cm}^{-1}$, i.e. noticeably less than expected from previous studies. In order to check for the origin of these two bonded N–H lines, we also checked that the RET dependency of anion formation does not depend on the IR laser wavelength. If these two lines would originate from two different dimer configuration, and if we selectively deplete one of these two isomer populations in the beam by setting the IR laser on one or the other N–H frequency, we should observe some variation in the RET anion formation rates as a function of the Rydberg quantum number. Nevertheless, we did not observe any such effect and the n -dependencies of the anion formation rates were all the same either without IR laser or when setting the laser frequency on either of the two bonded N–H lines.

Last but not least, we examine the C–H stretch region, which is, surprisingly, very rich and complex. From calculations, these modes are involved in few Fermi resonances with the amide modes at $1300\text{--}1700\text{ cm}^{-1}$. For instance, in the cyclic configuration, the second C–H stretch mode is calculated to be involved in a strong resonance with the in-plane NH_2 bending mode and one $\text{O}=\text{C}\text{--}\text{N}\text{--}\text{H}$ bending mode. However, these results cannot quantitatively account for all the observed lines and our interpretation rather relies on the comparison with another well-studied cyclic dimer: the formic acid dimer. In several beam [18] or matrix [19] experiments and theoretical [20] studies, the same kind of broad band with still several individual absorption peaks has been observed and discussed for the O–H stretch vibration. The interpretation is that this mode is coupled to a manifold of combination bands via Fermi resonances, leading to a broad absorption band extended over more than 200 cm^{-1} [18]. In particular, the O–H bend and $\text{C}=\text{O}$ stretch modes are strongly coupled to the O–H stretch due to the cooperatively strengthened double H-bond. In the case of a cyclic formamide dimer, the same multiple couplings between stretching modes and various bending modes are expected to produce the same broadening of the IR spectrum in the same region, i.e. $2700\text{--}3100\text{ cm}^{-1}$. It is quite surprising that the broad structure is limited to the C–H stretch region, and does not extend much up to the N–H stretch region at 3200 cm^{-1} , but this may be explained by the fact that all Fermi resonances involve only C–H and lower frequency modes. Eventually, this broad and complicated spectrum is a further indication of the predominance of the cyclic double H-bond structure for the formamide dimer.

All above experimental and theoretical data thus lead to the conclusion that the observed IR spectrum corresponds to the cyclic formamide dimer. Since this dimer configuration cannot be predissociated by one IR photon, one can wonder why we still observe a depletion of the anion signals. The first answer is the same as for the monomer: autodetachment should also occur for the dimer as for any vibrationally excited species. However, the observed depletions are more intense in the dimer spectrum, even for the free N–H stretch that corresponds to similar absorption intensity. Even if a total predissociation is not possible, one of the two H-bonds is probably broken by the IR photon absorption. As a result, those IR-excited neutral dimers are not anymore cold and cyclic but rather floppy with large-amplitude intermolecular motions. The corresponding weakly bound anions may thus not be formed at the same Rydberg quantum number and are probably highly unstable. Due to the intermolecular motions, the dipole (or quadrupole) moments vary and thus also the excess electron binding energy. This probably leads to a strong coupling between the intermolecular and excess electron motions that lead to fast and efficient autodetachment.

4. Summary and conclusions

The present data constitute further test results using our original spectroscopic technique that allows for monitoring IR absorption with rigorous mass selection of neutral polar species through very weakly bound anion formation. They show that this technique can be applied not only to weakly bound molecular complexes, for which vibrational predissociation is possible and fast, but also to isolated molecules or more strongly bound complexes. In the first case, vibrational autodetachment of the very weakly bound anions is responsible for the depletion of the anion signals. In the second case, the observed spectrum seems to originate only from the cyclic structure of the dimer. Since the dissociation energy of this double H-bond complex is higher than the absorbed photon energy, autodetachment is probably also the main process leading to anion depletion. It is reinforced by the fact that IR photon absorption can break one of the two H-bonds, leading to hot dimers with large intermolecular motions which are well coupled to the excess electron motion.

While the formamide monomer spectrum is straightforward and in excellent agreement with previous experimental data [10], the dimer spectrum displays many lines and a broad absorption band in the C–H stretch region, from 2800 to 3100 cm^{-1} , similar to that of the formic acid dimer [18–20] that is also a cyclic double H-bond complex. This also confirms the

previous assignment in matrix experiments [17], in which single H-bond complexes were also present. Moreover, the positions of two neighbouring bonded N–H stretch lines and the free N–H stretch line are in very good agreement with quantum chemistry calculations.

Further work with the same technique will concern N–methylformamide–water complexes in which three neutral configurations are expected, among which two isomers possess almost the same total dipole moment so that they cannot be distinguished by dipole-bound anion formation [7]. It will be interesting to see whether the contribution of these two expected isomers will appear in the IR spectrum.

References

- [1] E.G. Robertson, J.P. Simons. *Phys. Chem. Chem. Phys.*, **3**, 1 (2001).
- [2] B.C. Dian, J.R. Clarkson, T.S. Zwier. *Science*, **303**, 1169 (2004).
- [3] B. Lucas, F. Lecomte, B. Reimann, H.D. Barth, G. Grégoire, Y. Bouteiller, J.P. Schermann, C. Desfrancois. *Phys. Chem. Chem. Phys.*, **6**, 2600 (2004).
- [4] C. Desfrancois, J.P. Schermann. *Chem. Soc. Rev.*, **31**, 269 (2002).
- [5] C. Desfrancois, H. Abdoul-Carime, J.P. Schermann. *Int. J. modern. Phys.*, **10**, 1339 (1996).
- [6] K. Buchhold, B. Rieman, S. Djafani, H.D. Barth, B. Brutschy, P. Tarakeshwar, K.S. Kim. *J. chem. Phys.*, **112**, 177 (2000).
- [7] F. Lecomte, B. Lucas, G. Grégoire, J.P. Schermann, C. Desfrancois. *Eur. Phys. J. D*, **20**, 449 (2002).
- [8] C. Desfrancois, V. Périquet, S. Carles, J.P. Schermann, L. Adamowicz. *Chem. Phys.*, **239**, 475 (1998).
- [9] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Pet, J.A. Pople. Gaussian 03, Gaussian Inc. Pittsburg PA.
- [10] D. McNaughton, C.J. Evans, S. Lane, C.J. Lane, J. Nielsen. *J. mol. Spec.*, **193**, 104 (1999).
- [11] S.T. King. *J. phys. Chem.*, **75**, 405 (1971).
- [12] C.G. Bailey, C.E. Dessent, M.A. Johnson. *J. chem. phys.*, **104**, 6976 (1996).
- [13] A.A. Stuchebrukhov, M.V. Kuzmin, V.N. Bagratashvili, V.S. Letokhov. *Chem. Phys.*, **107**, 429 (1986).
- [14] D.J. Nesbitt, R.W. Field. *J. phys. Chem.*, **100**, 12735 (1996).
- [15] C. Desfrancois, Y. Bouteiller, J.P. Schermann, D. Radisic, S.T. Stokes, K.H. Bowen, N.I. Hammer, R.N. Compton. *Phys. Rev. Lett.*, **92**, 083003 (2004).
- [16] H. Abdoul-Carime, C. Desfrancois. *Eur. Phys. J. D*, **2**, 149 (1998).
- [17] M. Rasanen. *J. mol. Struct.*, **102**, 235 (1983).
- [18] F. Ito, T. Nakagana. *Chem. Phys.*, **277**, 163 (2002).
- [19] M. Halupka, W. Sander. *Spectrochim. Acta A*, **54**, 495 (1998).
- [20] G.M. Florio, T.S. Zwier, E.M. Myshakin, K.D. Jordan, E.L.S. Siebert III. *J. chem. Phys.*, **118**, 1735 (2003).