

Report on a visit to Institute for Optics Technical university of Berlin through the JSPS Core to Core Program

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As part of the JSPS Core to Core program, I studied in Prof. Otto Dopfer's research group in Institut für Optik und Atomare Physik Technische Universität Berlin for two weeks, from November 1st, 2011 to November 14th, 2011. This is report of my stay.

1. Aim of this work

In our laboratory, 4-aminobenzonitrile / water (1:1) cluster, which is abbreviated as ABN-W hereafter, is being investigated to observe the water migration induced photo-ionization. ABN has two binding site for water, one is amino group, and another is nitrile group (Fig. 1).

Actually, two kinds of cluster, a water molecule binds to amino group or nitrile group, coexist in

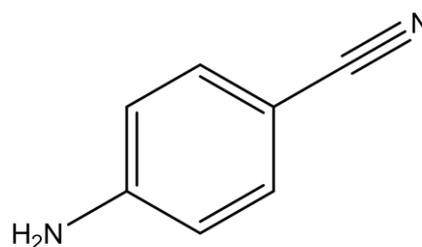


Fig. 1 The formula of ABN

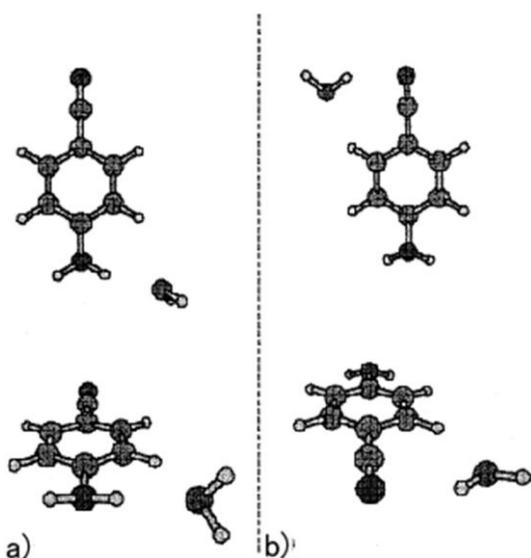


Fig. 2 Structure of ABN-W (1:1) cluster, a) NH structure and b) CN structure^{1,2}

the neutral ground state (Fig. 2).^{1, 2} The oxygen atom of water is bonded to an amino hydrogen atom in isomer (a) (NH structure), while in isomer (b) a hydrogen atom of water is bonded to the π electron cloud of the cyano nitrogen (CN structure).

Each isomer can be discriminated by IR spectrum, because they give completely different IR spectra. Fig. 3 shows IR spectra of ABN-W cluster. The IR spectrum of ABN monomer is shown in Fig. 3a for comparison. Fig. 3b and 3c correspond to the IR spectra of NH structure and CN structure of ABN-W

cluster in neutral ground state, respectively. In the NH structure, NH symmetric stretching vibration is red shifted about 20 cm^{-1} than monomer due to the hydrogen bond with water molecule, while in the CN structure, the NH band is observed at the same position as the monomer, which clearly shows that the amino group does not form the hydrogen bond.

We also measured IR spectra of ABN-W cluster in the cationic state (Fig 3d and 3e), and found that each cationic cluster generated by photo-ionization of each isomer gives the same IR spectrum, which is assigned to NH structure. This result suggests that CN structure isomer isomerizes to NH structure by the photo-ionization. To confirm this interpretation, it is important to clarify that the most stable isomer in the cationic state is NH structure. In Prof. Dopfer's laboratory, the most stable cationic clusters can be generated by an electro-impact ionization source and the IR spectra can be measured by IR photo dissociation method. In this work, we measured IR spectra of ABN-W cationic clusters to confirm that the most stable isomer is the NH structure.

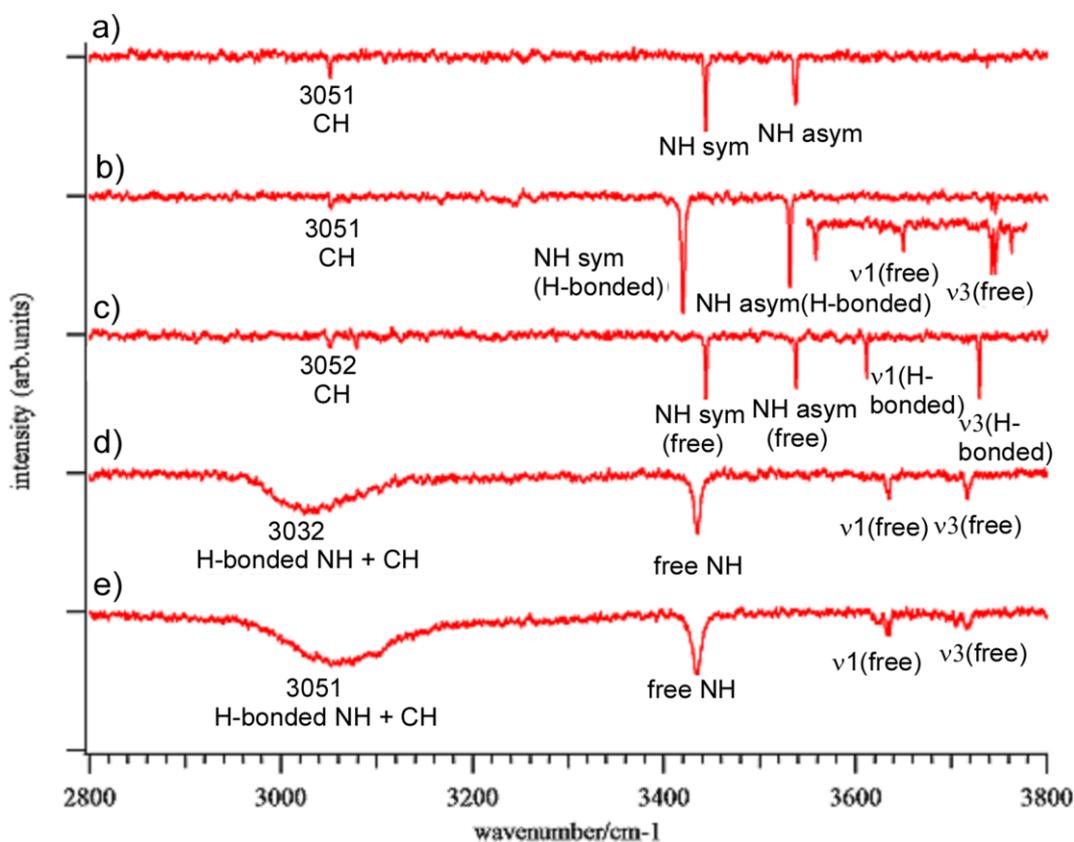


Fig. 3 IR-dip spectra of ABN and ABN-W^[3], a) monomer, b) NH structure, c) CN structure, d) NH structure (photo ionization), e) CN structure (photo ionization)

2. Experimental

Figure 4 shows a schematic diagram of experimental setup. The neutral molecules are ionized before the skimmer by electro-impact ionization. By collisions of the cationic molecules with water molecules and carrier Ar gas atoms, the cationic clusters are generated.

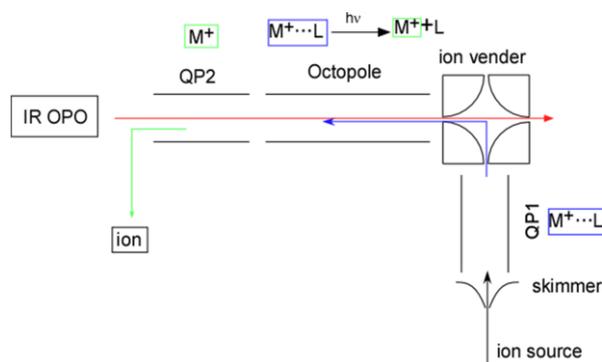


Fig.4 Experimental setup

The cationic clusters are passed

through a first quadrupole mass filter (QP1) to select a single mass species. Then, the selected cluster is bent at a right angle by an ion bender electrode and introduced into an octopole ion guide. Here, An infrared laser is introduced to the octopole ion guide. When the cluster is vibrationally excited due to the IR absorption, it dissociates into some fragment ions, one of which is selected by a second quadrupole mass filter (QP2) and detected by a dynode converter ion detector (Daly detector). The signal intensity should be proportional to the IR absorption cross section. Thus, by monitoring the fragment intensity as a function of the IR wavelength, we can obtain the IR photo dissociation (IRPD) spectrum of the size selected cluster cation.

3. Result & discussion

3.1 ABN⁺-Ar_n clusters

The IRPD spectroscopy detects IR absorptions as dissociations of clusters due to vibrational pre-dissociation. Thus, in principle, only vibrational levels higher than binding energy of the cluster can be observed. The binding energy of ABN⁺-W cluster is about 5000 cm⁻¹ therefore X-H stretch vibrations around 3000 cm⁻¹ are not observed in principle. To overcome this problem, not ABN⁺-W but ABN⁺-W-Ar cluster is measured. The binding energy between Ar and ABN⁺ is 500~800 cm⁻¹, so the X-H stretch vibrations can be observed through the Ar dissociation channel. Because the Ar atom acts as a messenger to carry the information of IR absorptions, this method is called “messenger method”. Thus, prior to the experiments of the ABN⁺-W cluster, we measured IR spectra of ABN⁺-Ar_n clusters for comparison.

Fig. 5 shows IRPD spectra of ABN-Ar_n → ABN (n = 1-3). In the all spectra, a band at ~3273 cm⁻¹ is observed, which is assigned to an overtone of bending vibration of NH₂ according to results of aniline.[4] On the other hand, frequencies and spectral features of two bands observed around 3370 and 3460 cm⁻¹, which are assigned to symmetric and

anti-symmetric stretching of NH_2 (ν_{NHs} and ν_{NHa}) on the basis of their frequencies, are different with the cluster size.

In $n = 1$ cluster, ν_{NHs} and ν_{NHa} are observed at 3372 and 3466 cm^{-1} with blue-side tails. This spectral feature closely resemble that of aniline⁺-Ar cluster, in which peaks of each band are observed at 3381 and 3477 cm^{-1} , respectively, with the blue-side tails.[4] In aniline⁺-Ar cluster, these two peaks are assigned to ν_{NHs} and ν_{NHa} of H bound isomer, in which Ar atom attaches to hydrogen atom of NH, while the blue-side tails are assigned to those of π bound isomer, in which Ar atom sits on the π -cloud of benzene ring. From the spectral similarity, we assigned the two intense peaks at 3372 and 3466 cm^{-1} to hydrogen bonded ν_{NHs} and ν_{NHa} of H bound isomer (Fig. 6a), and the blue-side tails to free ν_{NHs} and ν_{NHa} of π bound isomer (Fig. 6b). Similarly to aniline Ar (1:1) cluster cation, it is expected that the H bound isomer is more stable than the π bound isomer also in ABN-Ar cluster cation.

In the spectrum of $n = 2$, the peaks of ν_{NHs} and ν_{NHa} are observed at 3366 and 3450 cm^{-1} , respectively, which are red-shifted from those of $n=1$. This red-shift can be explained by HH bound structure, i.e. two Ar atoms attach to different hydrogen atom of NH_2 . The red-shifts of ν_{NHs} and ν_{NHa} from $n = 1$ to 2 are 6 and 16 cm^{-1} , respectively. Also in aniline⁺-Ar₂ cluster, the HH bound structure is a major isomer, and the corresponding shifts are 8 and 15 cm^{-1} , respectively.[4] That tendency is very similar to ABN⁺-Ar₂ cluster. Other peaks are observed at 3376 and 3468 cm^{-1} , which are close to ν_{NHs} and ν_{NHa} of H bound isomer of $n = 1$ cluster. Thus, these peaks are assigned to ν_{NHs} and ν_{NHa} of π H bound isomer, in which one Ar atom attaches to a hydrogen atom of NH_2 and another sits on the benzene ring.

Similarly, ν_{NH_s} and ν_{NH_a} are observed at 3366 and 3450 cm^{-1} in $n = 3$ cluster. However, no peaks corresponding to the $\text{H}\pi$ bound isomer are observed. Thus, these results suggest that both hydrogen atoms of NH_2 attach to Ar atoms in $n = 3$ cluster. The positions of two Ar atoms are determined, however, where is one more Ar atom? The

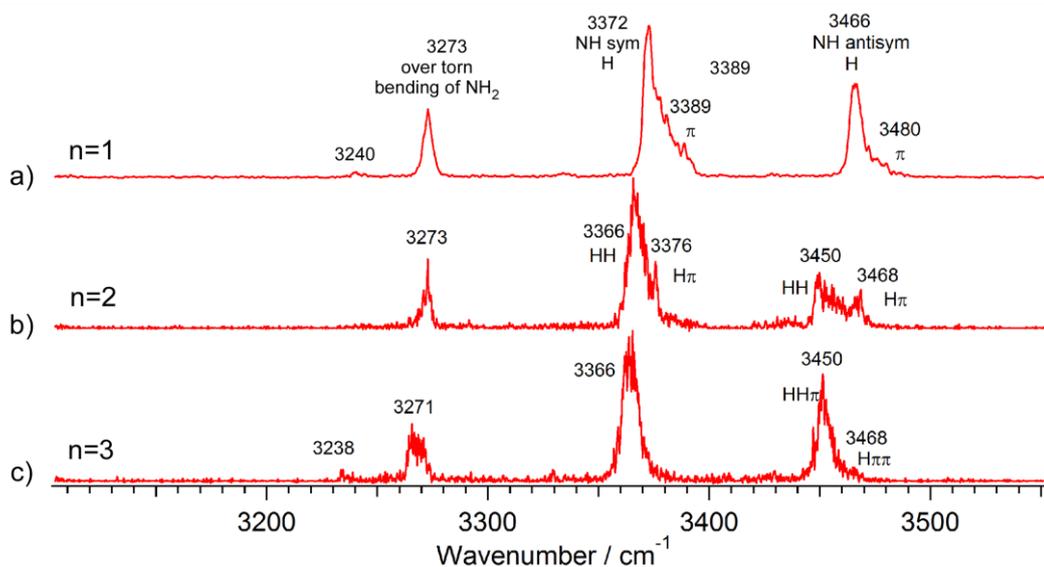


Fig. 5 IRPD spectra of $\text{ABN-Ar}_n \rightarrow \text{ABN}$ ($n = 1-3$)

possible position is top of the benzene ring or end of Ar atom bonding to hydrogen atom of NH_2 . The latter case will lead an enhancement of the hydrogen bond between Ar

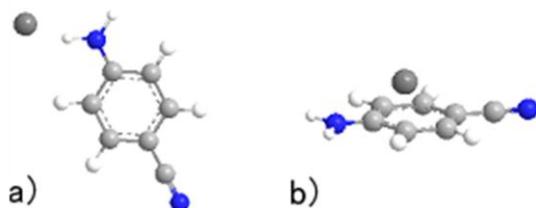


Fig. 6 Structure of ABN-Ar (1:1) cluster, a) H bound isomer and, b) π bound isomer

atom and NH, which should cause ν_{NH_s} and ν_{NH_a} more red-shift. However, the observed frequencies of ν_{NH_s} and ν_{NH_a} are the same with those of HH isomer of $n = 2$ cluster. Thus, it is expected that $n = 3$ cluster adopts $\text{HH}\pi$ structure. To confirm this interpretation, quantum chemical calculations should be carried out.

3.2 $\text{ABN}^+\text{-W}$ cluster

Fig. 7a shows IRPD spectrum of $\text{ABN-W} \rightarrow \text{ABN}$. As mentioned in the previous section, the IRPD spectrum lower than about 5000 cm^{-1} should not be observed by monitoring $\text{ABN-W} \rightarrow \text{ABN}$ channel. However, as the figure showing, the IRPD spectrum can be measured practically. Such a phenomenon can be observed generally in the IRPD spectroscopy, and is explained by initial internal energy of cation cluster. If

cation cluster has enough internal energy, $\sim 2000\text{ cm}^{-1}$, such hot cluster can dissociate by IR absorption. Thus, by monitoring $\text{ABN-W} \rightarrow \text{ABN}$ channel, we can measure the IR spectrum of hot ABN-W ensemble selectively. To obtain the cold spectrum, we measure $\text{ABN-W-Ar} \rightarrow \text{ABN-W}$ channel, i.e. messenger method. Fig. 7b shows IRPD spectrum of ABN-W measured by messenger method. By comparing both spectra, it was found that 1) two bands observed at 3630 and 3716 cm^{-1} , which are assigned to ν_1 and ν_3 vibrations of water, are sharpened, 2) ν_{NH_a} observed at 3431 cm^{-1} is red-shifted to 3418 cm^{-1} and 3) largely red-shifted ν_{NH_s} , which clearly shows that water molecule binds to NH site, is sharpened and red-shifted in the Ar tagging spectrum. The change of the spectral feature in the Ar tagging spectrum can be rationalized by the small internal energy of the Ar tagging cluster. Narrow bandwidth reflects narrow thermal distribution due to low temperature, and red shift of the hydrogen bonded NH stretching indicates that the hydrogen bond is strengthened by reducing the motion of water molecule. In either case, the observed spectra clearly demonstrates that the most stable isomer of ABN-W cluster cation is NH structure.

Next, we compared the IRPD spectrum of Ar tagging ABN-W cluster cation with IR spectrum of NH structure cation generated by laser ionization (Fig. 7c). The latter spectrum was measured by monitoring decreases of ion current of ABN-W due to the vibrational pre-dissociation. Thus, situation is the same with IRPD spectroscopy, that is, if the cluster does not have enough internal energy, the dissociation does not occur even if the cluster is excited by the IR laser. Therefore, the observed spectrum is that of hot clusters. Nonetheless, observed bandwidth of ν_{NH_a} , ν_1 and ν_3 are as narrow as or narrower than the corresponding bands observed in the IRPD spectrum. This may be because the thermal distribution of the initial ensemble is different between the electro-impact and laser ionizations. The laser ionization may give narrower distribution to initial states of the generated ion than the electro-impact ionization, because the distribution of the initial states generated by the laser ionization should be determined by Franck-Condon factor, and Franck-Condon active levels is fewer than the accessible levels by the electro-impact ionization, which does not have a limitation as the laser ionization in principle. On the other hand, the bandwidth of ν_{NH_a} of Fig. 7c is much broader than Fig. 7b, and is structure less. This result suggests that hydrogen bonded NH stretching forms strong anharmonic couplings in the hot clusters.

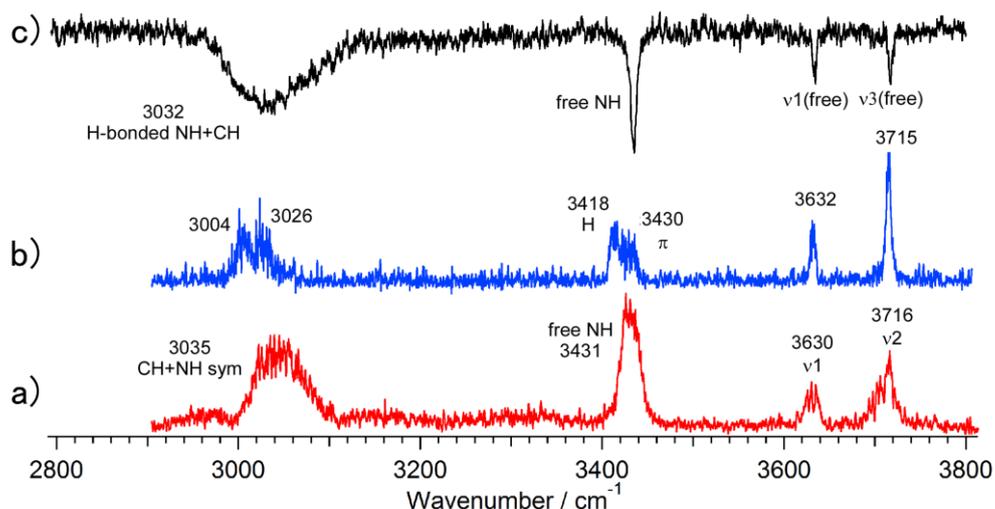


Fig. 7 IRPD spectra of ABN-W cluster a) $\text{ABN-W} \rightarrow \text{ABN}$, b) $\text{ABN-W-Ar} \rightarrow \text{ABN-W}$, c) NH^+ (laser ionization)

3.3 $\text{ABN}^+\text{-W}_{2,3}$ cluster

For future investigations, we also measured IRPD spectra of $\text{ABN-W}_n \rightarrow \text{ABN-W}_{n-1}$ and $\text{ABN-W}_n\text{-Ar} \rightarrow \text{ABN-W}_n$ ($n = 2, 3$) (Fig. 8). In $n = 2$ cluster, free NH stretch vibration is not observed, which suggests that each water molecule binds to each NH of amino group (Fig. 9a). On the other hand, a slightly broad band observed at $\sim 3400 \text{ cm}^{-1}$ in $n = 3$ cluster. This band can be assigned to hydrogen bonded OH stretching of a water molecule. Thus, it is expected that the $n = 3$ cluster has a structure such that one more water molecule binds to OH of a water ligand of $n = 2$ cluster (Fig. 9b). To confirm

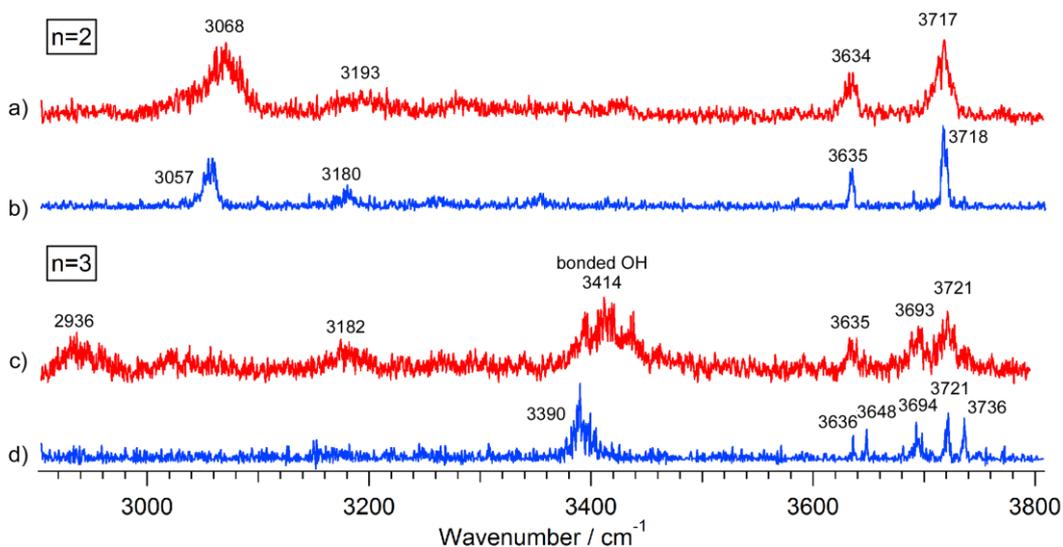


Fig. 8 IRPD spectra of ABN-W cluster a) $\text{ABN-W}_2 \rightarrow \text{ABN-W}_1$, b) $\text{ABN-W}_2 \text{ Ar} \rightarrow \text{ABN-W}_2$, c) $\text{ABN-W}_3 \rightarrow \text{ABN-W}_2$, d) $\text{ABN-W}_3 \text{ Ar} \rightarrow \text{ABN-W}_3$

these assignments, quantum chemical calculations will be incredible and is one of future works.

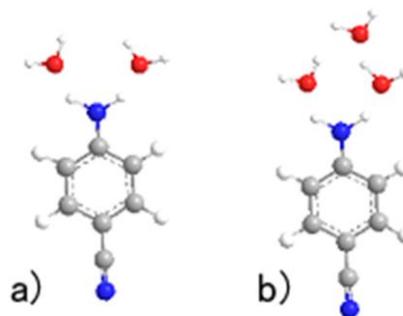


Fig. 9 Structure of a) ABN-W₂ and b) ABN-W₃

4. Summary and future works

We measured IRPD spectra of ABN-Ar_n, ABN-W_n and ABN-W_n-Ar (n = 1~3). In the all clusters, it was found that the amino group is the most stable binding site in cationic state. To determine the assignments of observed IR spectra, quantum chemical calculations are indispensable. From this collaboration study, it was experimentally confirmed that the most stable isomer of ABN⁺-W cluster is NH structure. The picosecond experiment will be a very curious study to clarify details of the water migration dynamics which takes place by laser ionization of CN isomer of neutral ABN-W cluster.

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References

- [1] K. Sakota, N. Yamamoto, K. Ohashi, M. Saeki, S. Ishiuchi, M. Sakai, M. Fujii and H. Sekiya, *Chem. Phys.*, **2002**, 283, 209.
- [2] K. Sakota, N. Yamamoto, K. Ohashi, M. Saeki, S. Ishiuchi, M. Sakai, M. Fujii and H. Sekiya, *Phys. Chem. Chem. Phys.*, **2003**, 5, 1775.
- [3] experimental data of Nakamura
- [4] N. Solcá and O. Dopfer, *Eur. Phys. J. D*, **2002**, 20, 469.