

Evidence for Chiral Isomers in the Spectra of Small Size Selected Hydrazine Clusters

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Dedicated to Prof. Dr. Dr. h. c. mult. H. Gg. Wagner on the occasion of his 70th birthday

(Received December 21, 1999; accepted January 17, 2000)

Molecular Clusters / IR-Spectra / Calculations of Lineshifts

New configurations of hydrazine (N_2H_4)_n clusters have been calculated from dimer to tetramer which contain one monomer with one inverted NH_2 group. This procedure generates new chiral isomers of the clusters. The calculated lineshifts of the asymmetric NH_2 wag mode lead for the dimer and the trimer to a much better agreement with the experimental results than obtained in previous calculations without the chiral isomers. For the tetramer the spectra do not differ for the two configurations.

Für Hydrazin-Cluster (N_2H_4)_n vom Dimer bis zum Tetramer wurden neue Konfigurationen berechnet, bei denen in einem Molekül eine NH_2 -Gruppe invertiert wurde. Dies ergibt neue chirale Isomere dieser Cluster. Die berechneten Linienverschiebungen der NH_2 -Biegeschwingungen des Dimers und Trimers sind in besserer Übereinstimmung mit den Messdaten als frühere Rechnungen ohne die chiralen Isomere. Für die Tetramere gibt es keine Unterschiede.

1. Introduction

The photodissociation of weakly bound clusters has attracted much interest in recent years. In these experiments a vibrational mode of the molecular components is excited by infrared laser radiation. If the photon energy is larger than the binding energy of the cluster, the complex will typically dissociate according to the coupling of the molecular modes to the cluster motion. The observed vibrational dissociation spectra contain detailed information on the structure and on the absorption and decay dynamics. While

the latter topic requires high resolution spectroscopy in order to analyze the linewidth correctly [1] or direct time resolved studies [2], the structural information can also be obtained from the lineshift in low resolution experiments. This is especially valid, if the investigated clusters are selected according to their size [3, 4]. Experiments along these lines have been carried out for a number of systems using the momentum transfer in a scattering experiment with atoms for size selection. For the excitation either a linetunable CO₂ laser or an optical parametric oscillator (OPO) in the infrared are used for the excitations. The available results have been reviewed [5–9].

In order to get the structural information, the experimental data have to be compared with calculations of the frequency shifts as function of the cluster size. While the calculations of the lineshifts are well understood and practical methods are available, reliable predictions depend critically on the interaction potential. Systematic studies are therefore quite rare. One attempt is concentrated on methanol clusters for which aside from the CO stretch mode [10–12] also the OH stretch mode [13–15] has been observed experimentally and analyzed theoretically using different potential models [16–18]. Another example are hydrogen fluoride clusters [19]. Great interest is also concentrated on the OH stretch mode of water which has been thoroughly investigated [20, 21]. While most of these modes show large redshifts (OH) or very small blueshifts (CO), a completely different behavior is observed for the antisymmetric NH₂ wag mode in hydrazine. Here large blue shifts of more than hundred wavenumbers are obtained [5, 22, 23]. While an attempt to calculate these shifts using a standard potential model failed, we have recently published a new systematic potential for hydrazine clusters [24] for which these shifts were predicted correctly. The detailed analysis of the experiments which included also new data obtained with isotopically substituted CO₂ lasers [23] revealed that it proved necessary to take into account several isomers in the calculation for a complete interpretation of the data. But still there were some discrepancies left, especially what the interpretation of the dimer and trimer spectrum concerned.

In principle, the hydrazine molecule, which consists of two amino groups twisted against each other by 90°, can exist in two different chiral conformations, *s* and *r*, depending on the relative orientation of the NH₂ group with respect to the N–N bond. For the dimer, for example, we expect two different kinds of isomers of the *ss* and *sr* type to be formed. In the previous calculations only the *ss* type was taken into account. Here we present new calculations for clusters in which one molecule is chirally inverted. We investigate how these clusters behave and if they account for the discrepancies in the interpretation of the data.

The paper is organized as follows. We start with a short description of the calculation of the new minimum energy configurations followed by the calculation of the lineshifts of the three lowest energy isomers from the

Table 1. Lineshifts $\Delta\nu_{12}$ ($\nu_{12} = 937 \text{ cm}^{-1}$, NH_2 wag) calculated for the three lowest energy configurations of the R-clusters along with their intensities I (in D^2) using the systematic potential of Ref. [24]. The binding energies E of the clusters are given in kJ/mol .

n	E	$\Delta\nu$	I	E	$\Delta\nu$	I	E	$\Delta\nu$	I
2	-26.51	45.74	0.045	-18.90	19.01	0.039	-18.43	33.20	0.019
		51.31	0.000		46.46	0.006		38.65	0.026
3	-56.77	45.81	0.015	-56.22	47.92	0.028	-56.18	49.27	0.012
		64.40	0.043		75.65	0.038		72.51	0.052
		80.48	0.009		88.72	0.001		85.82	0.003
4	-93.81	61.83	0.003	-93.69	58.49	0.004	-93.65	68.12	0.008
		79.93	0.022		73.41	0.032		83.45	0.047
		79.36	0.049		84.17	0.024		84.77	0.021
		99.75	0.015		103.14	0.030		104.56	0.014

dimer to the tetramer. Then the results are compared with the experiments and the paper closes with a discussion of the results.

2. Calculations

2.1 Structure calculations

The structure calculations follow exactly the procedure described in Ref. [24] and, basically, imply minimizing the total interaction energy of the cluster, considered as being composed of rigid molecules. For the interaction the systematic model potential of Wheatley is used, with the parameters given in the cited article. The potential is calculated from properties of the monomers and contains the electrostatic interaction using a distributed multipole expansion and a penetration component, the repulsion, and the attractive induction and dispersion terms [25]. To find the local minima of the potential energy, the positions and orientations of all molecules (specified by the Cartesian coordinates of their center of mass and by Euler angles) are optimized without constraints starting from random initial configurations. Typically, several thousands of minimizations are necessary to yield the global minimum for a particular cluster size.

As already pointed out, we consider clusters composed of both energetically equivalent isomeric species under which the hydrazine molecule can occur, designated as species *s* and *r*, respectively. In the case of species *s*, the upper NH_2 group can be viewed as being rotated counter-clockwise about the N-N axis with respect to the lower NH_2 group. In the case of species *r*, the rotation is clockwise. Technically, to obtain from the structure

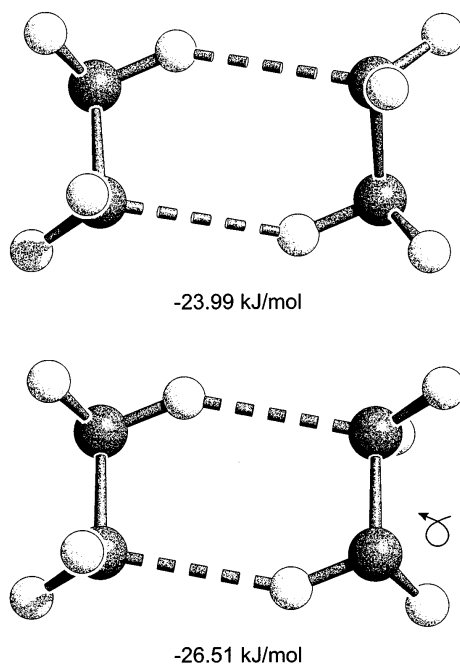


Fig. 1. The energetically most stable hydrazine dimer structures for the S- (upper panel) and the R-configuration (lower panel). The inverted amino group is marked by a curly arrow.

of monomer species *s* the structure for species *r*, the Cartesian coordinates of all atoms have to be inverted. The cluster structures implying this species will be referred to as R-clusters. They cover in the context of this work the clusters *sr*, *ssr*, and *sssr*. This nomenclature is obviously intended to suggest the presence of monomers of species *r* in the cluster structure as opposed to the S-structures which only contain *s* type monomers.

The results for the binding energies of the considered R-configurations are presented in Table 1. Some selected cluster structures are shown in Figs. 1–3, where they are compared with the corresponding S-complexes. The resulted lowest energy S-dimer configuration and the corresponding R-counterpart are shown in Fig. 1. The rotated amino group in the R-structure is the lower one in the right molecule, marked by the curly arrow. Here the R-form has inversion symmetry. The bonding energy (26.5 kJ/mol) is larger than that of the S-minimum (23.99 kJ/mol). This result is in good agreement with an *ab initio* calculation at the MP2 (Moller-Plesset perturbation theory second order) level which gives for a large basis set the values of 29.8 and 26.3 kJ/mol, respectively [26]. In the case of the second lowest energy minima, the bonding energy of the S-structure is larger than that of the

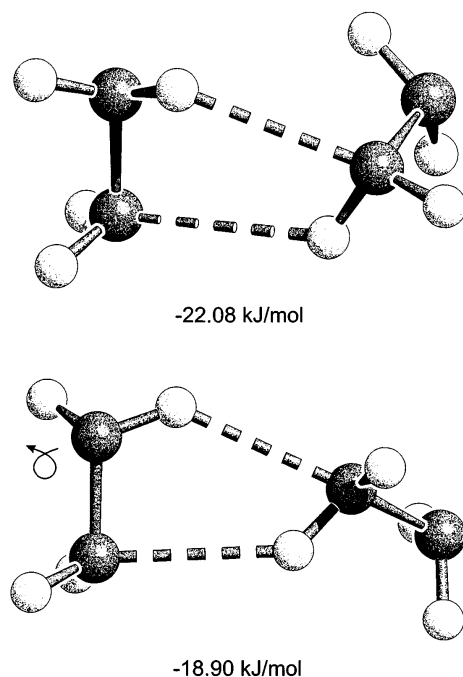


Fig. 2. The energetically second most stable hydrazine dimer structures for the S- (upper panel) and the R-configuration (lower panel). The inverted amino group is marked by a curly arrow.

corresponding R-minimum. The structures are shown in Fig. 2. Here the inversion of the upper amino group of the left molecule leads to a more strained geometry with less energy, 18.9 versus 22.1 kJ/mol. In Fig. 3 some results for the trimer are displayed. The lowest energy S-configuration has no comparable structure in the R-manifold. Therefore we compare here the lowest energy R-trimer with the *second* lowest S-trimer, previously calculated. Again the bonding energy of the R-trimer structure is larger, 56.8 versus 54.4 kJ/mol. Apparently the change in the geometry of the upper amino group of the upper right molecule leads to a change of the hydrogen bond to the lower N atom of the upper left molecule. In the case of the tetramer the structures of the two species become quite similar with minimum energies which agree within one percent. Thus, we did not find it necessary to show them.

2.2 Lineshifts

For determining the line shifts we have employed the same second order perturbation approach as in our previous calculations reported in Ref. [24].

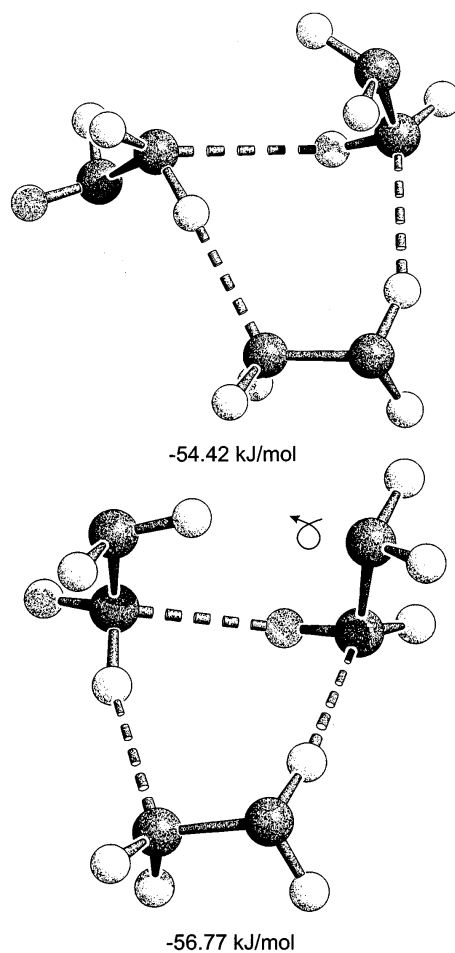


Fig. 3. Hydrazine trimer structures: upper panel: the energetically second most stable structure for the S-configuration; lower panel: the most stable R-configuration. The inverted amino group is marked by a curly arrow.

The basic idea is to treat the anharmonic intramolecular force field and the intermolecular potential as a quantum mechanical perturbation of the molecular vibrations, described in the normal mode approach [16, 27, 28]. The first order frequency shifts depend only on the curvature of the intermolecular potential, while the second order frequency shifts involve also the molecular cubic force constants, which describe the coupling of the considered mode to the other intramolecular modes.

The results based on the three lowest minimum energy configurations of the different R-clusters and the intramolecular force field of Ref. [29]

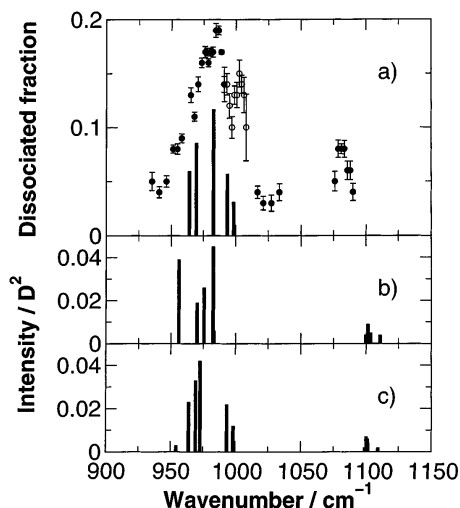


Fig. 4. a) Measured photodissociation spectra of hydrazine dimers [23] and calculated stick spectra based on the lowest energy R- and the two lowest energy S-configurations. b) Calculated stick spectra based on the three lowest energy R-configurations. c) Calculated stick spectra based on the three lowest energy S-configurations [23, 24].

are shown in Table 1. They are also plotted as stick spectra in panel b) of Figs. 1–3. The units are debye squared (D^2). For comparison, also the results obtained in Ref. [23, 24] for the S-clusters are presented in panel c).

3. Results and discussion

The molecular clusters studied in this paper, $(N_2H_4)_n$, and the excited vibrational mode, the asymmetric NH_2 wag at 937 cm^{-1} , are of special interest. First, this is one of the few well studied examples of a large amplitude *angular* motion which probes repulsive forces and leads to a large blueshift. Secondly, the question has to be answered up to what extent appear the R-isomers with inverted coordinates in the measured spectra. A first glance on the structures in Figs. 1–3 reveals only small differences to the ones with S-structure. The calculated lineshifts, however, clearly exhibit a different behavior for the dimer and, to a lesser extent, also for the trimer. In the case of the tetramer, the spectra are quite similar. Let us discuss the clusters separately. We note that the barrier for the interconversion of the S- and R-structures in the monomer is with 31.1 kJ/mol [30] so high that once the clusters are formed they will stay in their selected configuration.

The lowest energy configuration of the R-dimer, which is also the global minimum, is completely symmetric, so that only one line results with a shift

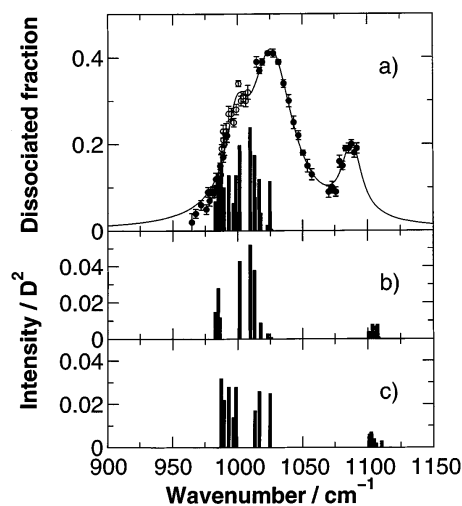


Fig. 5. a) Measured photodissociation spectra of hydrazine trimers [23] and calculated stick spectra based on the lowest energy R- and S-configurations. b) Calculated stick spectra based on the three lowest energy R-configurations. c) Calculated stick spectra based on the three lowest energy S-configurations [23, 24].

of 45.7 cm^{-1} . It belongs to the collective motion of the free H atoms, while the motion of the bound H atoms is not infrared active. In contrast, the lowest energy configuration of the S-dimer gives lineshifts of 32.3 and 61.4 cm^{-1} , corresponding to the free and the hindered motion of the H atoms. For the second lowest energy configuration the S-isomer, which in this case is deeper than the R-isomer, nearly the same shifts of 26.8 cm^{-1} and 56.6 cm^{-1} are obtained. Here the R-isomer shows smaller shifts of 19.0 and 46.5 cm^{-1} which are caused by a less stronger bonding.

For the comparison with the experimental data we only take into account the contributions of the three lowest energy contributions, the lowest energy R-dimer and the two lowest energy S-dimers. This is justified by the large energy difference between this group (26.5 to 22.1 kJ/mol) and the following isomers (18.9 to 17.56 kJ/mol). Based on these results, which are displayed in Fig. 4a, we get a nearly perfect agreement with the spectrum. Now the origin of the three peaks at 978 (41), 985 (48), and 1002 (65) cm^{-1} is easily interpreted. The peak at the largest frequency at 1002 cm^{-1} originates from the motion of the hydrogen bonded H atoms of the lowest and second lowest energy configuration of the S-dimers. The next peak at 985 cm^{-1} is caused by the motion of the free H atoms of the lowest energy R-dimer and the shoulder at 978 cm^{-1} and the subsequent fall off of the intensity is composed of the motion of the free H atoms of the lowest two energy configurations of the S-dimer. The good agreement

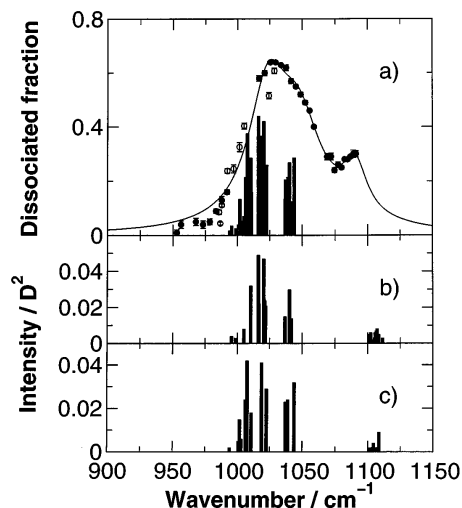


Fig. 6. a) Measured photodissociation spectra of hydrazine tetramers [23] and calculated stick spectra based on the lowest energy R- and S-configurations. b) Calculated stick spectra based on the three lowest energy R-configurations. c) Calculated stick spectra based on the three lowest energy S-configurations [23, 24].

of the maximum of the spectrum with the prediction based on the lowest energy R-dimer is a direct indication that this isomer is present in the cluster beam.

For the trimer the calculation of the line shifts also exhibits a different behavior of the S- and the R-isomers. The former ones are characterized by two groups of lines separated by a gap around 1010 cm^{-1} . The group at larger wavenumbers consists of three lines originating from the H bonded molecules of the three lowest energy forms, while to the group at smaller wavenumbers the free molecules of the configurations contribute two lines each. The R-isomers have their maximal intensities exactly in the intensity gap of the S-isomers. This contribution originates from the motion of quasi-free H atoms which are slightly hindered by their environment. In the present case the energy differences between the S- and the R-conformations are within 5 percent, so that we take them all into account in the comparison with the experimental data, shown in Fig. 5a. The agreement with the data is improved by adding the contribution of the R-isomers. Their maximum intensity appears just in the range where the curve has a pronounced shoulder. Here the intensity distribution is not matched. The intensities of the main peak and the shoulder are reversed in the calculation. In spite of this deviation the comparison reveals that the R-trimers are also present in the cluster beam.

In the case of the tetramer, the intensity distribution of the lineshifts of the S- and the R-isomers are quite similar, although not identical. Both reproduce the measurements quite well. Here the three-dimensional structure offers so many possible sites for the hydrogen bonding that the additional variation introduced by the R-version does not lead to new combinations.

In conclusion we note that the contributions of the R-clusters of the type sr, ssr, and sssr with one molecule with inverted coordinates improves the agreement with the measured spectra appreciably. For the dimer, the peak intensity of the spectrum is completely accounted for. For the trimer the intensity gap observed in the previous calculations is filled.

The general interpretation which was already obtained in the previous papers did not change. The dimers form chainlike arrangements with two hydrogen bonds. The trimers appear as cyclic configurations with one donor/acceptor hydrogen bond per molecule. All the larger clusters are composed of three-dimensional arrangements. In all cases more than one isomer is necessary to reproduce the data. The agreement between theory and experiment is quite remarkable in view of the fact that the calculation of the systematic interaction potential is, so to speak, the first attempt and not adjusted to any experimental data. There are some deviations in the prediction of the absolute intensity of the trimer, although the structural pattern is well reproduced. This could be a problem of the simplified model with which the transition probability is calculated, although it works better for the dimer and the tetramer. In any case, the reproduction of the measured data is remarkable and we conclude that also the R-cluster structures found in this analysis definitely contribute to the measured data.

Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft and the Alexander-von-Humboldt-Stiftung through the "Forschungskoooperation Europa". We thank Dr. V. Dyczmons and Professor P. Botschwina for the *ab initio* calculation of the hydrazine dimer and for sharing the results with us prior to publication. We are grateful to Dr. R. Wheatley and Dr. V. Dyczmons for pointing out to us the existence of chiral isomers.

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