Frequency shifts in infrared spectra of ethylene clusters

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In recent years, infrared photodissociation spectroscopy has emerged into a promising experimental tool for the investigation of molecular clusters.[1] One of the prototype systems is the vibrational predissociation of ethylene $(C_2H_4)_n$ clusters upon absorption of infrared radiation in the region of the fundamental excitation of the ν_7 mode. Pioneering experiments showed a broad absorption band with a width in the order of 10 cm^{-1}.[2,3] The maximum of this spectral feature was found to be shifted by 3 cm^{-1} toward higher frequencies with respect to the monomer absorption at 949 cm^{-1}. Later, experiments with size selected clusters (ranging from the dimer to the hexamer) revealed that this blue shift amounts, regardless of the cluster size, to 3 cm^{-1}.[4–7]

In order to explain this remarkable result, structure calculations of ethylene clusters were carried out. A pairwise potential was constructed with the help of the test-particle method.[8] For details of the intermolecular potential function, the interested reader is referred to another publication by the authors.[9] Using this model, structures for the dimer, trimer, and tetramer were obtained by minimizing the total interaction energy of the ethylene clusters.

Binding energies ΔE and point symmetry groups of the most important isomers for these cluster sizes are given in Table I. The situation for the dimer is a clearcut case. Each molecule is bound by two H atoms to the π-electron clouds of its partner. This prediction for the structure is also confirmed in a recent *ab initio* study.[10] Analogously, this type of crosswise arrangement is also found in chainlike trimers and tetramers. In each case, the binding energy is about 6.9 kJ/mol per each van der Waals bond. The symmetry is D_{2d} or D_{2h} for chains of even or odd length, respectively. For the trimer and the tetramer, there are also more compact, ringlike structures of C_3 (trimer) and S_4 (tetramer) symmetry. With their respective binding energies of $\Delta E = 14.3$ kJ/mol and $\Delta E = 25.1$ kJ/mol they are 3% (trimer) and 20% (tetramer) more stable than the corresponding chainlike isomers.

In an attempt to relate the experimental finding of a constant frequency shift of the ν_7 mode to the results of the structure calculations, the question of the relative abundances of these species had to be addressed. Using a harmonic oscillator/rigid rotor model, free energies of the ringlike and chainlike isomers were calculated.[9] For the trimer, it was shown that the chain/ring ratio remains below a value of 1:2 for all temperatures up to 300 K. For the tetramer, this ratio exceeds unity at a temperature of about 150 K. However, a clear interpretation was hampered by two principal difficulties: First, there are appreciable uncertainties in the estimation of cluster temperatures in molecular beams, and, secondly, the energies and/or dynamics of the dissociation process might be in favor of one of the isomers.

In order to attack the problem more directly, we try in the present work to provide spectroscopic evidence for the presence of either type of isomers in the experiments. Based on the structure calculations of ethylene clusters, shifts of the fundamental frequency of the ν_7 mode are calculated. Our theoretical treatment uses an approach in which the interaction of the molecules is treated as a (weak) perturbation acting on the normal mode Hamiltonian describing the uncoupled (degenerate) vibrations of identical molecules. To first order, the intermolecular potential causes a coupling of the ν_7 vibrations of the individual molecules to the collective vibrational modes of the cluster and thus removes the degeneracy of the excitation frequencies. It has to be noted that in case of symmetric clusters the degeneracy may be only partly or not at all removed (*vide infra*). Based on this approach, also relative infrared intensities can be obtained as the square of the transition dipole moment of the cluster vibrations. More details of the perturbation method can be found in a recent publication of the authors.[11]

In the frequency shift calculations presented here, only first order formulas have been applied.[12] The second order coupling of different vibrational modes induced by an interplay of the cubic anharmonicity and the interaction of the molecules is of no importance here, because the only symmetry-allowed cubic couplings of the symmetric CH_2 wagging ν_7 mode of B_{1u} symmetry[13] to the ν_1, ν_2, and ν_3 modes are negligible.[14] Our results for the frequency shifts and infrared intensities for the dimer and the various isomers of trimers and tetramers are compiled in Table I. There is a single ν_7 absorption of the ethylene dimer (D_{2d}) which is shifted by 1.1 cm^{-1} to the blue. Due to the high symmetry of the complex, the symmetric and antisymmetric combinations of the monomer vibrations are doubly degenerate, they trans-

TABLE I. Structure and spectra of ethene clusters. The first three columns give the binding energy ΔE and the point symmetry group for each of the isomers under investigation. The last three columns list the frequency shift $\Delta\nu_7$, the infrared intensity I (relative to the C_2H_4 monomer), and the irreducible representation for each of the infrared-active cluster vibrations.

Cluster	ΔE [kJ/mol]	Symmetry	$\Delta\nu_7$ [cm^{-1}]	I/I_{mono}	Irrep.
Dimer	6.87	D_{2d}	+1.1	2×1.0	E
Trimer[a]	14.29	C_3	+2.7	2×0.6	E
			+1.9	1.8	A
Trimer[b]	13.81	D_{2h}	+2.3	1.0	B_{3u}
			+1.4	2.0	B_{2u}
Tetramer[a]	25.10	S_4	+1.8	2.0	B
			+0.7	2×1.0	E
Tetramer[b]	20.76	D_{2d}	+2.3	2×1.5	E
			+1.0	2×0.5	E

[a]Ringlike arrangement.
[b]Chainlike arrangement.

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form according to the irreducible representation E. This situation changes for the larger clusters. In the calculated spectra of the trimers and tetramers, there are frequency splittings. The spectrum of the ringlike isomer of the trimer (C_3) exhibits two modes with a blue shift of 2.7 cm^{-1} (E) and 1.9 cm^{-1} (A), while that of the chainlike configuration (D_{2h}) consists of two frequencies with slightly smaller blue shifts of 2.3 cm^{-1} (B_{3u}) and 1.4 cm^{-1} (B_{2u}). In either case, the peak with the smaller blue shift carries more infrared intensity. The ratios are 3:2 and 2:1 for the ring and chain isomer, respectively. Also, the ν_7 excitation of the ringlike ethylene tetramer (S_4) is split. Our calculations yield blue shifts of 1.8 cm^{-1} (B) and 0.7 cm^{-1} (E). The shifts are somewhat larger for the chainlike isomer (D_{2d}) of this cluster where shifts of 2.3 cm^{-1} (E) and 1.0 cm^{-1} (E) can be found.

In the following, we want to summarize and discuss our results of the fundamental ν_7 excitation in small ethylene clusters (dimers to tetramer). In all cases we find blue shifts in the order of 1–3 cm^{-1}. The smallness of these shifts can be explained by two different reasons: First of all, the van der Waals interaction holding the ethylene clusters together is very weak. Moreover, the CH_2 wagging motion is not hindered very strongly. This is in contrast to the results for some heterogeneous clusters. The quasihydrogen bonded situation of ethylene–acetone complexes[12] and of ethylene–hydrogen halide dimers[15] gives rise to blue shifts in the order of 10–20 cm^{-1}. For these systems as well as for the clusters considered here, the intermolecular forces are always such that the effective force constants associated with the ν_7 mode are enhanced which explains the sign of the frequency shifts (blue shifts).

A closer inspection of our spectra of the chainlike isomers reveals some interesting features. For both the trimer and the tetramer, the mode with the larger blue shift (2.3 cm^{-1}) corresponds to vibrations of molecules in the inner positions of the chains. For longer and longer chains, this shift converges to approximately 3 cm^{-1} in the limit of a chain of infinite length. The lower absorption frequency of these isomers can be attributed to vibrations of molecules at the edges. The shift of this mode in the spectrum of the chainlike tetramer (1.0 cm^{-1}) is already equal to the infinite chain limit. For the trimer, however, this frequency is slightly higher (1.4 cm^{-1}). This deviation is caused by a symmetric coupling between the vibrations of the terminal molecules which are separated by only one molecule. It is interesting that also the frequency shift of the cross-type dimer (1.1 cm^{-1}) which is the basic unit of the chainlike oligomers fits these results very well. Unfortunately, the spectra of the ringlike isomers are not very different from those of the chainlike configurations. For the trimer, the blue shifts of the former ones are 0.5 cm^{-1} larger than those for the latter ones while for the tetramer they are roughly 0.5 cm^{-1} smaller. Therefore, a comparison of our calculated frequency shifts with the experimental spectra cannot be used to distinguish spectroscopically between the two isomeric forms found in the structure calculations of ethylene clusters. Both the extremely large width of the absorption bands and the limited tunability of the CO_2 laser prohibit an unambiguous statement about the abundances of ringlike or chainlike isomers in the molecular beam experiments. It is noted that high resolution experiments should be able to reveal the different behavior. The calculations presented here, however, can explain the two main experimental findings very well. First, the sign and magnitude of the shifts of the ν_7 excitation is in very good agreement. Secondly, for the clusters investigated here, these shifts do not vary with the cluster size.

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