

Structure and photodissociation spectra of mixed ethene–acetone clusters

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Infrared photodissociation spectra of the mixed complexes $C_2H_4-CH_3COCH_3$ and $C_2H_4-(CH_3COCH_3)_2$ have been observed after size selecting them by scattering from a helium beam combined with mass spectrometric detection. The excitation of the ν_7 -out of plane symmetric wagging mode of ethene near its gas phase frequency at 949.3 cm^{-1} with a cw- CO_2 laser leads to a characteristic depletion of the cluster beam. The dissociation spectrum of the 1:1 complex can be explained by two peaks at 950.8 and 961.6 cm^{-1} . Calculations of minimum energy configurations and band shifts based on an empirical site–site potential show that these frequencies can be attributed to the absorption of two different isomers. They correspond to the two different binding patterns of the H atoms of ethene to the O atom of acetone and those of acetone to the C–C group of ethene, respectively. For the 1:2 complex, a large peak at 958.5 cm^{-1} and a smaller one around 940.5 cm^{-1} are found which can be explained in a similar manner by several isomers found in the structure calculations.

I. INTRODUCTION

Spectroscopic investigations of small molecular clusters provide detailed information on interactions between molecules that determine both their microscopic and macroscopic behaviour, including phase transitions, crystal formation, and solvation effects.¹ The generation of these weakly bound complexes in supersonic expansions combined with laser spectroscopy is a powerful tool for these studies, since high intensities and low temperatures are provided. In a special class of experiments the absorption of radiation leads to vibrational predissociation which is detected by depletion of the signal.² A number of systems have been studied in this way, a prominent example being the ethene dimer, an object of intensive theoretical and experimental work.^{3–9} In many of these experiments CO_2 lasers are used to dissociate the clusters after excitation of the ν_7 out of plane symmetric CH_2 wagging mode (B_{1u}) of the ethene molecule. Within the resolution limit of $1\text{--}2\text{ cm}^{-1}$, only one broad Lorentzian shaped dissociation peak appears in the spectra that exhibits a blue shift of 3 cm^{-1} with respect to the monomer absorption at 949.3 cm^{-1} . This can be explained by the fact that the ν_7 vibration is not strongly disturbed by the weak van der Waals bond of the dimer. Later on, in high resolution experiments, also much smaller linewidths have been observed^{6–8} which are not yet fully understood.⁹

Nearly the same small shifts of 3 cm^{-1} are observed for larger size selected ethene clusters up to a cluster size of $n=6$.^{10,11} An attempt to interpret these results by structure calculations is given in Ref. 12. In another series of experiments, one of the constituents of the dimer is replaced by various atoms and molecules to investigate how the type of the bond and the number of internal degrees of freedom affects the dissociation behavior. The effect of single rare gas atoms like Kr, Ar, and Ne on the ν_7 mode was found to be quite small with resulting shifts of $\Delta\omega \leq 1\text{ cm}^{-1}$ to the blue.³ In a later experiment also some additional structure was observed.¹³ Such small shifts are to be expected for

weak van der Waals bonds with atoms. The quasi-hydrogen-bonded complexes C_2H_4-HCl and C_2H_4-HF , on the other hand, exhibit large blue shifts of 15 and 25.5 cm^{-1} , respectively, which result from a strong perturbation of the ethene vibration caused by a T-shaped structure with the hydrogen of the diatom strongly bound to the π -electron cloud of C_2H_4 .¹⁴

In this context we considered it interesting to investigate how another very common solvent molecule, acetone, would influence the ethene ν_7 vibration. Now an additional possible site arises for the bonding, namely, the interaction of the H atoms of the hydrocarbon C_2H_4 with the O atom of the carbonyl compound $(CH_3)_2CO$ which act as a proton donor and acceptor, respectively. For the related interaction of acetylene with formaldehyde a bridged planar form involving two nonlinear hydrogen bonds was found recently.¹⁵

Here we report the dissociation spectra of two mixed ethene–acetone complexes which we were able to detect and size select in our apparatus. These are $C_2H_4-CH_3COCH_3$ and $C_2H_4-(CH_3COCH_3)_2$, further simply referred to as “1:1” and “1:2” complex. It is also the first application of the method of size selection by atom scattering¹⁶ with subsequent infrared photodissociation spectroscopy^{17–19} to heterogeneous clusters. The spectra can be explained best by assuming the existence of different isomers of each cluster. Calculations with an empirical potential support this idea, since several minimum energy configurations are found in each case. A preliminary account of the results already appeared in conference proceedings.^{20,21} Here, we present, in addition, frequency shift calculations based on perturbation theory. In contrast to our earlier speculations,^{20,21} these calculations predict a large blueshift of $10\text{--}20\text{ cm}^{-1}$, if one or two hydrogen atoms of the ethene molecule are bound to the O atom of the acetone molecule and a smaller blue shift of $2\text{--}3\text{ cm}^{-1}$ for the configuration in which the hydrogen atoms of the acetone are bound to the π -electron cloud of the C–C double bond of ethene. The latter isomer also has a slightly lower bond-

TABLE I. Beam data.

	Mixture ^a	He
Nozzle diameter (μm)	150	30
Nozzle temperature (K)	300	300
Stagnation pressure (bar)	1.5	30
Peak velocity (m/s)	1368	1795
Speed ratio	23	65

^a9% C₂H₄, 10% CH₃COCH₃, 81% He.

ing energy. Similar calculations for homogeneous ethene clusters are also able to explain the experimental results obtained earlier¹⁰⁻¹² and will be published elsewhere.²²

II. EXPERIMENT

Our scattering machine provides two molecular beams which are crossed at 90° and which are rotatable around their intersection point. The fixed detector consists of an electron multiplier and a quadrupole mass filter with 70 eV electron impact ionization. The beam velocities are determined using a pseudo-random time of flight (TOF) setup. A detailed description is given in Ref. 23. The clusters are formed in an adiabatic expansion of a mixture of 9% ethene, 10% acetone, and 81% helium through a 150 μm nozzle at a stagnation pressure of 1.5 bar. To obtain this gas composition that worked best for our purpose, a 10% mixture of ethene in helium is connected to a steel cylinder containing acetone cooled to 14 °C to get the appropriate vapor pressure. The beam data are listed in Table I.

It is well known that the mass spectrometer is not sufficient to select a certain cluster size from the distribution that is produced in the expansion, since the ionization process leads to fragmentation. That means that every ion mass peak contains an unknown amount of fragments of larger parent clusters and only those with masses below the tuned ion mass are excluded from the signal. For this reason we use the scattering by a rare gas beam to discriminate against the larger neutral clusters as follows: With the measured beam velocities and the known masses of the clusters, a maximum elastic scattering angle can be calculated for each cluster size. At a fixed detection angle, all clusters exceeding a certain limiting mass are kinematically excluded. A specific cluster is now isolated by setting the detector above the limiting angle of the next larger size and tuning the mass filter to a mass higher than that of the next smaller neutral cluster.¹⁶ This procedure works well unless the difference of the limiting angles of adjacent cluster sizes falls below 0.5°. In Table II all possible mixed clusters of ethene and acetone up to $m=232$ u are listed with their calculated limiting angles. Figure 1 shows a mass spectrum of the scattered cluster beam at a laboratory (lab) angle of 3° at which all clusters with masses larger than 230 u are excluded. By comparison with a mass spectrum of an acetone-helium beam and the well known fragmentation pattern of ethene,²⁴ the observed mass peaks can be assigned as shown in Table III. The only mixed clusters within this mass region that appear on their parent masses are C₂H₄-CH₃COCH₃ at $m=86$ u and C₂H₄-

TABLE II. Limiting scattering angles of the mixed ethene-acetone clusters.

n_{ethene}	n_{acetone}	mass (u)	Θ (deg)
2	0	56	12.0
3	0	84	8.0
1	1	86	7.8
4	0	112	6.0
2	1	114	5.9
0	2	116	5.8
5	0	140	4.8
3	1	142	4.8
1	2	144	4.7
6	0	168	4.0
4	1	170	4.0
2	2	172	3.9
0	3	174	3.9
7	0	196	3.4
5	1	198	3.4
3	2	200	3.4
1	3	202	3.3
8	0	224	3.0
2	3	230	2.9
0	4	232	2.9

(CH₃COCH₃)₂ at $m=144$ u. Therefore, if we detect them on these masses, contributions of smaller mass combinations as given in Table I are ruled out. To exclude possible fragments from larger clusters, the measurement is carried out at detection angles 1° above the limiting angles of the next larger complex. In this way the 1:1 complex is detected at 7°, 0.8° below its own limiting angle because of a larger signal. For the 1:2 cluster, still sufficiently large signals are found at 5°, 0.3° above the elastic scattering limit due to the limited angular resolution. Thus in both cases the experimental conditions are well satisfied for a pure size selection.

A cw-CO₂ laser with an output power of 7 W, corresponding to an average fluence of 21 mJ/cm² in this arrangement, is coupled collinearly into the scattered beam

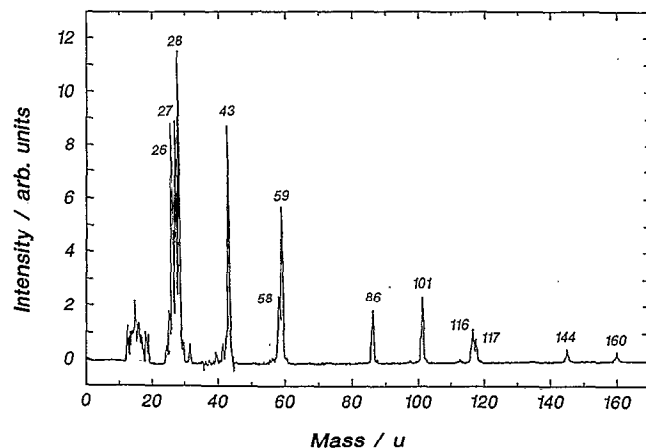


FIG. 1. Mass spectrum of the scattered cluster beam taken at 3° which includes masses up to 230 u. Aside from many known fragment ions of ethene and acetone, two peaks at $m=86$ u and $m=144$ u appear that are assigned to C₂H₄-CH₃COCH₃ and C₂H₄-(CH₃COCH₃)₂.

TABLE III. Composition of the ionized cluster beam.

Mass (u)	Fragment ion
15	CH ₃ ⁺
26	C ₂ H ₃ ⁺
27	C ₂ H ₃ ⁺
28	C ₂ H ₄ ⁺
41	C ₃ H ₅ ⁺
43	CH ₃ CO ⁺
58	CH ₃ COCH ₃ ⁺
59	CH ₃ COCH ₃ H ⁺
86	CH ₃ COCH ₃ C ₂ H ₄ ⁺
101	CH ₃ COCH ₃ CH ₃ CO ⁺
116	(CH ₃ COCH ₃) ₂ ⁺
117	(CH ₃ COCH ₃) ₂ H ⁺
144	(CH ₃ COCH ₃) ₂ C ₂ H ₄ ⁺
160	(CH ₃ COCH ₃) ₂ CH ₃ COH ⁺

and dissociation spectra are recorded by tuning the laser through the 10 μm transitions from 920 to 990 cm^{-1} . A small pyroelectric detector inside the machine is used to record the fluence on all laser lines for later normalization. A detailed description of this laser setup can be found in Ref. 25.

III. DISSOCIATION SPECTRA

Assuming a single photon dissociation process, the fraction of dissociated clusters can be expressed corresponding to Beer's law by

$$P_{\text{diss}}(\nu) = 1 - \exp[-\sigma(\nu)F/h\nu], \quad (1)$$

where ν is the laser frequency, F the laser fluence, and $\sigma(\nu)$ the dissociation cross section. In an approximation based on perturbation theory and Fermi's golden rule, this cross section is given by

$$\sigma(\nu) = \frac{8\pi^2\nu}{c} |\langle f | \mathbf{me} | i \rangle|^2 \frac{\Gamma_d}{(h\nu - h\nu_0)^2 + (\Gamma_d)^2} \quad (2)$$

with $|i\rangle$ being the ground state of the complex, $|f\rangle$ the vibrationally excited state, and \mathbf{me} the product of the transition dipole moment and the laser polarization, describing the infrared absorption process.²⁶ The dissociation rate Γ_d depends on the coupling of the excited state $|f\rangle$ to the states of the dissociation continuum $|s\rangle$ of the ground state that is caused by the intermolecular potential V

$$\Gamma_d = \frac{\pi}{\hbar} |\langle s | V | f \rangle|^2. \quad (3)$$

We are aware of the fact that this formula was originally derived for dissociation from a single rovibrational state of a long-lived complex. Since for most of the ethene containing complexes the dissociation spectra could be fitted by a single broad Lorentzian line, we assume that the same mechanism also works for the systems investigated here. It cannot be decided at the moment, at least as long as no high resolution data are available, if the lines are homogeneously broadened or represent an inhomogeneous contribution from an unresolved band structure. The measured dissociation spectra in the 3 μm range in which a

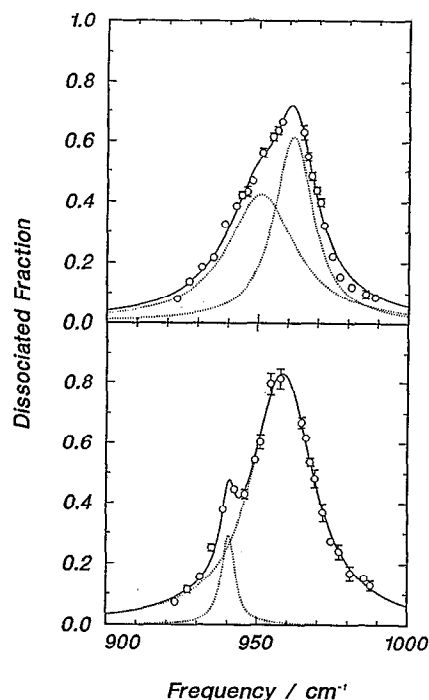


FIG. 2. Infrared dissociation spectra of the clusters C₂H₄-CH₃COCH₃ (upper part) and C₂H₄-(CH₃COCH₃)₂ (lower part). The solid lines are fits based on two Lorentzians (dotted curves).

high resolution F-center laser is used show that they are apparently dominated by homogenous broadening.⁵ Based on this background, our discrete depletion spectra are fitted by a sum of Lorentzian lines which represent different isomers. Each of them is characterized by three fitting parameters: the maximum dissociation cross section σ_0 , the center frequency ν_0 , and the line width Γ (FWHM).

Figure 2 displays both the experimental and the fitted spectra of the mixed ethene-acetone clusters. The fitting parameters are listed in Table IV. In both cases it was impossible to fit the spectrum with a single Lorentzian although there is only one ethene molecule present that can absorb infrared radiation in this frequency interval. We do not believe that the CH₃-rocking mode of acetone whose monomer absorption occurs at 891 cm^{-1} would be blue-shifted by nearly 60 cm^{-1} in these clusters, since no dissociation of pure acetone dimers was observed around 950 cm^{-1} . All remaining infrared active acetone vibrations occur at even more distant frequencies. Therefore the only explanation for the two peaks is the existence of isomers of each complex. To investigate this problem more closely, we

TABLE IV. Fitted Lorentzian parameters of the measured dissociation spectra.

Cluster	ν_0 (cm^{-1})	σ_0 (10^{-18}cm^2)	Γ (cm^{-1})
C ₂ H ₄ -CH ₃ COCH ₃	950.8	0.49	24.3
	961.6	0.86	12.4
C ₂ H ₄ -(CH ₃ COCH ₃) ₂	940.5	0.31	5.1
	958.5	1.59	16.2

carried out some structure calculations that are reported in the next section.

IV. STRUCTURE CALCULATIONS

Since the large size of the complexes considered here renders an *ab initio* calculation too time consuming and expensive, we use the empirical potential EPEN/2 (*empirical potential based on the interaction of electrons and nuclei*). It was designed by Scheraga and co-workers²⁷ to describe the conformational behavior of a wide range of inorganic and organic molecules. In this model, every molecule is represented by a rigid arrangement of positively charged nuclei, placed at the positions of the atoms, and negatively charged so-called "electrons" that approximately reflect the electron distribution. They also act as centers of non-electrostatic interactions. In this model the total potential energy is given by

$$E_{\text{pot}} = \sum_{i,j} q_i q_j \left[\frac{1389.35}{r_{ij}} + A_{ij} \exp(-B_{ij} r_{ij}) - \frac{C_{ij}}{r_{ij}^6} \right]. \quad (4)$$

If the charges q_i are measured in elementary charges and the distances r_{ij} in Å, the total intermolecular energy of the molecules results in kJ/mol. It is the sum of interaction energies between all pairs of sites i and j that do not belong to the same molecule. The parameters A_{ij} , B_{ij} , and C_{ij} are derived from the characteristic parameters of each site following the simple combination rules

$$A_{ij} = \sqrt{A_i A_j},$$

$$B_{ij} = (B_i + B_j)/2,$$

$$C_{ij} = \sqrt{C_i C_j}.$$

The parametrization was optimized by least square fits to spectroscopic, crystallographic, and thermodynamic data.

Based on this potential model, a quasi-Newton minimization algorithm was applied to find the minima of the multidimensional energy surface.³⁰ The monomer geometries of acetone and ethene were taken from Refs. 28 and 29, respectively. The position and orientation of each of the rigid molecules were described by six coordinates each, the three components of the center-of-mass displacement vector and three Eulerian angles. Starting from random configurations, several hundred minimization runs were performed for each cluster size. The results are displayed in Figs. 3 and 4 for the two complexes and the corresponding binding energies are given in Table V. For the 1:1 complex, two different types of isomers appear in which the bonding takes place either between the hydrogen atom(s) of ethene and the O atom of acetone or the hydrogen atom(s) of the acetone molecule and the π -electron cloud of ethene. The calculated binding energies of 13.92 and 12.55 kJ/mol lie somewhere between pure van der Waals systems such as $(\text{C}_2\text{H}_4)_2$ (6.9 kJ/mol) (Ref. 12) and strongly hydrogen-bonded systems like the acetone dimer (24.3 kJ/mol). A further stable dimer with a binding energy of more than 3 kJ/mol smaller than the most stable one has been found in the calculations. It is probably not present in the cold nozzle beam expansion. However, since we did not perform

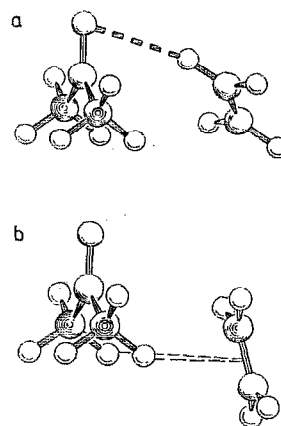


FIG. 3. Calculated minimum energy configurations of the mixed dimer $\text{C}_2\text{H}_4\text{-CH}_3\text{COCH}_3$. The binding energies are given in Table V. Hydrogen bonds are marked by dashed lines.

Monte Carlo or molecular dynamics calculations to simulate the process of thermal averaging occurring for finite temperatures, no precise prediction can be made about the population of these minima at realistic beam temperatures.

The 1:2 complexes have binding energies around 38 kJ/mol which can be rationalized by adding the binding energies of an acetone dimer, which gives in the present potential model 24.3 kJ/mol, and the energy of the acetone-ethene complex of about 14 kJ/mol. Thus the most stable structures essentially look like an acetone dimer with an ethene molecule attached to it. In structure (c) the ethene is in exactly the same position as in the heterogeneous dimer (a), while going from structure (h) to (a) the ethene moves from the outside of the acetone dimer between the two acetone molecules. In (h), one of the H atoms of ethene is bound to an O atom of acetone, whereas in (a) an additional bond between the π cloud of ethene and an H atom of the second acetone molecule occurs. Moreover, configurations like (d) and (f) are found in which two H atoms of ethene are bound to each of the O atoms of acetone. In structure (f) the acetone dimer configuration with its two hydrogen bonds is almost lost and kind of cyclic structure of the three molecules results.

V. CALCULATION OF FREQUENCY SHIFTS

Based on the minimum energy configurations of the 1:1 and 1:2 complexes discussed above, shifts of the fundamental excitation frequency of the ν_7 mode of the ethene molecule are calculated. We make use of a formula developed by Buckingham to describe the change of the vibrational energy levels of a chromophore under the influence of a solvent environment.³¹⁻³³ Assuming that the intermolecular potential U is considerably weaker than the intramolecular force field, the former can be treated together with the anharmonic part of the force field as a quantum mechanical perturbation acting on the normal mode vibrations. If we are dealing with heterogeneous clusters containing only one molecule which carries infrared activity in the spectral region under investigation (here C_2H_4) and if

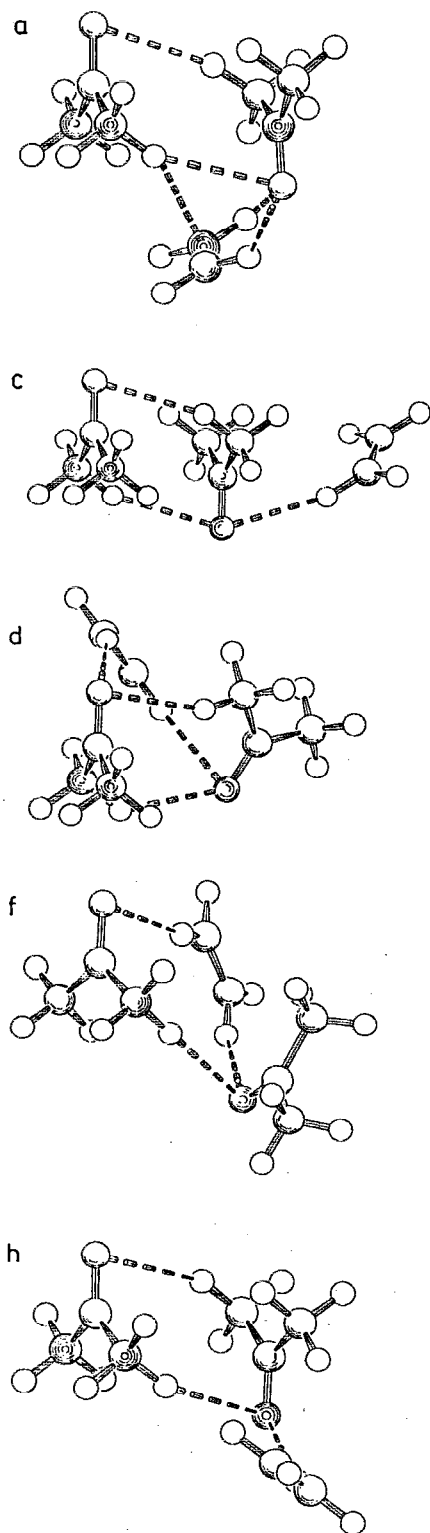


FIG. 4. Calculated minimum energy configurations of the mixed trimer $C_2H_4-(CH_3COCH_3)_2$. The binding energies are given in Table V. Hydrogen bonds are marked by dashed lines.

the mode to be excited is nondegenerate, the formalism of non-degenerate perturbation theory can be applied to second order. The resulting shift of the frequency ν_i (measured in wave numbers) of the fundamental excitation of this molecule is given by

TABLE V. Theoretical and experimental line shifts of the mixed clusters.

Cluster		E (kJ mol $^{-1}$)	$\Delta\nu_{\text{theor}}$ (cm $^{-1}$)	$\Delta\nu_{\text{exp}}$ (cm $^{-1}$)
$C_2H_4-CH_3COCH_3$	<i>a</i>	-13.92	+12.0	+12.3
	<i>b</i>	-12.55	+2.6	+1.5
$C_2H_4-(CH_3COCH_3)_2$	<i>a</i>	-38.88	+3.1	+9.2
	<i>c</i>	-37.62	+12.1	
	<i>d</i>	-36.32	+21.5	
	<i>f</i>	-35.95	+19.1	
	<i>h</i>	-35.44	+7.1	

$$\Delta\nu_i = \frac{1}{2hc} \left(\frac{\partial^2 U}{\partial q_i^2} - \sum_{j=1}^{3N-6} \frac{\phi_{ij}}{\nu_j} \frac{\partial U}{\partial q_j} \right) \quad (5)$$

in which the q_j stand for the $3N-6$ dimensionless normal coordinates of an N -atomic molecule and the ϕ_{ij} are the cubic force constants defined in the basis of these coordinates. They describe the coupling between the normal modes i and j . The derivatives of the form $\partial U/\partial q$ denote partial derivatives of the intermolecular potential U with respect to the normal coordinates q . They are taken by keeping the position of the center of mass and the orientation of the molecules constant. When modeling the interaction potential U in a site-site approximation as is described earlier, these derivatives are calculated most easily numerically by stepwise displacing the atomic sites following the motion of the respective normal coordinate.

The first expression on the right hand side of Eq. (5) is the first order contribution to the shift: It gives the direct change of the force constant associated with the normal coordinate q_i which is caused by the intermolecular binding. The second part of the band shift formula denotes the second order contributions: The summation over all modes j indicates a coupling of all normal modes induced by the off-diagonal cubic force constants ϕ_{ij} . By identifying the expression $-\partial U/\partial q_j$ with a force acting along the j th normal coordinate, this contribution to the frequency shift can be interpreted as an indirect change of the force constant.

For symmetric molecules, however, the scheme of cubic coupling may simplify considerably.³³ Because the symmetric CH_2 wagging ν_7 mode of the ethene molecule transforms according to the irreducible representation B_{1u} , only the constants ϕ_{77j} with $j=1,2,3$ are nonvanishing. They describe the anharmonic coupling to the three modes of in plane vibration which transform like A_g . They are estimated using the *ab initio* calculations of Ref. 34. Their values indicate that the coupling to the CH stretching and to the CH_2 scissors motion is extremely small. The only remaining coupling to the CC stretching mode is not of importance here, because there are no strong forces acting on the CC bond for the complexes under investigation. Therefore, the second order contributions to the frequency shifts are neglected completely and the simplified formula

$$\Delta\nu_i = \frac{1}{2hc} \frac{\partial^2 U}{\partial q_i^2} \quad (6)$$

is used for the ν_7 band shift calculations. For more details the interested reader is referred to Ref. 35. In this way all calculated configurations were investigated using, of course, the same potential function as for the structure calculations. The results are shown in Table V in comparison with the experimental data. They clearly demonstrate that each of the different structural isomers exhibits a different spectral shift so that it should be possible to distinguish them by their spectra.

VI. DISCUSSION

Concerning the generation of mixed ethene-acetone clusters in a molecular beam expansion, a distribution of all possible compositions from pure ethene to pure acetone complexes is expected. In the mass spectra, however, no ions containing more than one ethene molecule appear at the nominal cluster masses. This means that they are either completely fragmented upon ionization or that they are too unstable to be formed in the expansion. The latter can be understood regarding the fact that the binding energy of acetone dimers (24 kJ/mol) exceeds that of the ethene dimer (6.9 kJ/mol) by more than a factor of 3. The structure calculations further suggest that both pure acetone clusters and mixed clusters with one ethene are bound by weak hydrogen bonds rather than by van der Waals forces.

For the 1:1 complex, the results of the frequency shift calculations agree quite well with the experimental results and strongly support the suggestion to attribute the two observed dissociation peaks to two different isomers as is done in Table V. This is also confirmed by double resonance experiments with two CO_2 lasers, in which one laser was tuned to one of the dissociation peaks and the other was used to record the spectrum in the usual way.³⁶ These experiments clearly indicate that the two peaks belong to two different isomers. The calculations provide, in addition, also information on which isomer is responsible for which shift. The mixed dimer with a binding energy of 12.55 kJ/mol, in which the ethene molecule is bound by its π -electron cloud to the H atoms of the acetone is shifted by only 2.6 cm^{-1} . For the other isomer of the heterodimer with 13.92 kJ/mol, a larger shift of 12.0 cm^{-1} occurs, because here one of the H atoms is directly bound to the O atom of acetone which strongly hinders the vibrational motion of the excited ethene and thus causes the blueshift.

This shows that the ν_7 frequency depends more sensitively on the actual cluster geometry than on the strength of the intermolecular bond. Therefore, predictions are quite difficult to make. This can be further illustrated by the fact that the complex $\text{C}_2\text{H}_4\text{-HF}$ (Ref. 14) shows a blueshift of 25.5 cm^{-1} as opposed to 2.6 cm^{-1} for the mixed ethene-acetone dimer (b), although in both cases the ethene molecule is bound by its π -electron cloud to H atoms. In case of the trimer, the results are a little more complicated. As can be seen in Table V, the five most stable isomers exhibit also different band shifts which range from +3.1 to +21.5 cm^{-1} . The measured dissociation spectrum, however, is dominated by one large peak with a blueshift of 9.2 cm^{-1} and a small peak shifted to the red by more than 8 cm^{-1} . The large peak can be attributed

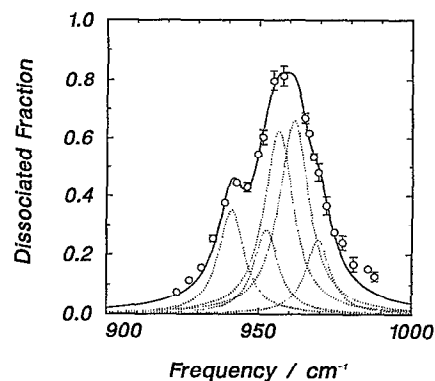


FIG. 5. Alternative fit to the trimer spectrum based on the calculated frequency shifts of the different isomers. Based on the calculated frequencies of four isomers (see the text) and constant band widths of 9 cm^{-1} throughout, only the dissociation cross sections, proportional to the height of the Lorentzians, were fitted.

to isomer (c). There is, however, a larger discrepancy between the calculated frequency of the other isomers and the observed, redshifted small peak in the spectrum. In addition, the peak widths are quite different so that the large peak can also be interpreted in a different way as follows. In order to account for the other calculated isomers, the spectrum was fitted with constraint frequency shifts and band widths of 9 cm^{-1} using the theoretical band centers of Table V. The result is displayed in Fig. 5. The agreement between measured and calculated points is aside from some points around 985 cm^{-1} at least as good as in the unconstrained fit of Fig. 4. The result can be interpreted as population analysis of the different isomers in the actual experimental expansion conditions. Isomers (c) and (h) are the most frequent ones ($\sigma_0=0.88$ and 0.96, respectively) followed by a smaller fraction of roughly the same amount of (a) ($\sigma_0=0.30$) as well as the similar structures (d) and (f), centered around a shift of +20 cm^{-1} ($\sigma_0=0.26$).³⁷ There is, in addition, the red shifted peak ($\sigma_0=0.39$) which is not explained in this analysis and which might be caused by another isomer that was not found in the calculations. Perhaps this question could be solved by double resonance experiments or Monte Carlo simulations of the spectra.

The frequency shifts of the different isomers can be qualitatively rationalized by their corresponding structures. As expected, isomer (c) behaves very similar to the dimer (a). The hindered H atom motion of the ethene bound to the O atom leads to a blue shift of 12 cm^{-1} . The change of the position of the ethene molecule with respect to the acetone dimer in isomer (h) and (a) leads to a more free motion of the H atoms and a smaller blue shift of 7.1 and 3.1 cm^{-1} , respectively. In case of the isomers (d) and (f), two H atoms instead of one are involved in the binding to the two O atoms of the acetone molecules and, consequently, a larger blue shift of about 20 cm^{-1} is found.

In summary, the coexistence of different isomers has been demonstrated for 1:1 and 1:2 complexes of ethene and acetone reflecting the different possibilities of hydrogen

bonding to the O atom of acetone and the π -electron cloud of ethene. This was achieved in a combined effort of vibrational predissociation experiments in the infrared with size selected neutral clusters, structure calculations using site-site model potentials and calculations of the spectral shifts based on perturbation theory. For the mixed dimer, the two expected isomers are found. In case of the mixed trimers, we have to distinguish between different bonds of the ethene molecule to the acetone dimer which range from that between the π electrons of ethene and the H atoms of acetone to that between one or two H atoms of ethene and the O atom of acetone.

ACKNOWLEDGMENTS

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- ¹The complete issue No. 9 of *Ber. Bunsenges. Phys. Chem.* **96** (1992).
- ²R. E. Miller, *Science* **240**, 447 (1988).
- ³M. P. Casassa, D. S. Bomse, and K. C. Janda, *J. Chem. Phys.* **74**, 5044 (1981).
- ⁴M. A. Hoffbauer, K. P. Liu, C. F. Giese, and W. R. Gentry, *J. Chem. Phys.* **78**, 5567 (1983).
- ⁵G. Fischer, R. E. Miller, and R. O. Watts, *Chem. Phys.* **80**, 147 (1983).
- ⁶K. G. H. Baldwin and R. O. Watts, *J. Chem. Phys.* **87**, 873 (1986).
- ⁷B. Heijmen, C. Liedenaum, S. Stolte, and J. Reuss, *Z. Phys. D* **6**, 199 (1987).
- ⁸U. Buck, C. Lauenstein, A. Rudolph, B. Heijmen, S. Stolte, and J. Reuss, *Chem. Phys. Lett.* **144**, 396 (1988).
- ⁹S. R. Hair, J. A. Beswick, and K. C. Janda, *J. Chem. Phys.* **89**, 3970 (1988).
- ¹⁰U. Buck, F. Huisken, C. Lauenstein, H. Meyer, and R. Sroka, *J. Chem. Phys.* **87**, 6276 (1987).
- ¹¹F. Huisken and T. Pertsch, *J. Chem. Phys.* **86**, 106 (1987).
- ¹²R. Ahlrichs, S. Brode, U. Buck, M. DeKieviet, Ch. Lauenstein, A. Rudolph, and B. Schmidt, *Z. Phys. D* **15**, 341 (1990).
- ¹³C. M. Western, M. P. Casassa, and K. C. Janda, *J. Chem. Phys.* **80**, 4781 (1984).
- ¹⁴M. P. Casassa, C. M. Western, F. G. Celii, D. E. Brinza, and K. C. Janda, *J. Chem. Phys.* **79**, 3227 (1983).
- ¹⁵N. W. Howard and A. C. Legon, *J. Chem. Phys.* **88**, 6793 (1988).
- ¹⁶U. Buck and H. Meyer, *Phys. Rev. Lett.* **52**, 109 (1984); *J. Chem. Phys.* **84**, 4854 (1986).
- ¹⁷U. Buck, in *The Chemical Physics of Atomic and Molecular Clusters*, edited by G. Scoles (North-Holland, Amsterdam, 1990), p. 543.
- ¹⁸U. Buck, in *Dynamics of Polyatomic van der Waals Complexes*, edited by N. Halberstadt and K. C. Janda (Plenum, New York, 1990), p. 43.
- ¹⁹F. Huisken, *Adv. Chem. Phys.* **81**, 63 (1991).
- ²⁰U. Buck, X. J. Gu, M. Hobein, C. Lauenstein, and A. Rudolph, *J. Chem. Soc. Faraday Trans.* **86**, 1923 (1990).
- ²¹U. Buck, X. J. Gu, M. Hobein, R. Krohne, C. Lauenstein, H. Linnartz, and A. Rudolph, *Z. Phys. D* **20**, 177 (1991).
- ²²U. Buck and B. Schmidt (unpublished).
- ²³U. Buck, F. Huisken, J. Schleusener, and J. Schäfer, *J. Chem. Phys.* **72**, 1512 (1980).
- ²⁴U. Buck, C. Lauenstein, H. Meyer, and R. Sroka, *J. Phys. Chem.* **92**, 1916 (1988).
- ²⁵U. Buck, X. J. Gu, Ch. Lauenstein, and A. Rudolph, *J. Chem. Phys.* **92**, 6017 (1990).
- ²⁶J. A. Beswick, in *Structure and Dynamics of Weakly Bound Complexes*, NATO ASI Series, edited by A. Weber (Reidel, Dordrecht, 1987), p. 563.
- ²⁷J. Snir, R. A. Nemenoff, and H. A. Scheraga, *J. Chem. Phys.* **82**, 2497 (1978).
- ²⁸D. J. Frurip, L. A. Curtiss, and M. Blander, *J. Chem. Phys.* **82**, 2555 (1978).
- ²⁹P. Pulay, *J. Mol. Spectrosc.* **40**, 59 (1971).
- ³⁰The quasi-Newton algorithm used in the multidimensional minimization was the program E04JAF from the NAG library.
- ³¹U. Buck and B. Schmidt, *J. Mol. Liquids* **46**, 181 (1990).
- ³²A. D. Buckingham, *J. Chem. Soc. Faraday Trans.* **56**, 753 (1960).
- ³³P. O. Westlund and R. M. Lynden-Bell, *Mol. Phys.* **60**, 1089 (1987).
- ³⁴G. Fogarsi and P. Pulay, *Acta Chim. Acad. Sci. Hung.* **108**, 55 (1981).
- ³⁵U. Buck and B. Schmidt, *J. Chem. Phys.* **98**, 9410 (1993).
- ³⁶U. Buck and M. Hobein, *Z. Phys. D* (1993).
- ³⁷The dissociation cross sections are given in units of 10^{-18} cm².