Sub-Doppler High-Resolution Spectra of C_6H_6: Anomalous Results in the "Channel Three" Region

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We have measured the Doppler-free rotationally resolved two-photon spectrum of two vibronic bands of C_6H_6, $14_0^1 \, 1_0^1$ and $14_0^1 \, 1_0^2$. Compared to the $14_0^1 \, 1_0^1$ band ($E_{excess} = 2492$ cm^{-1}) a drastically reduced number of sharp lines is observed in the $14_0^1 \, 1_0^2$ band ($E_{excess} = 3412$ cm^{-1}). The $K = 0$ rotational lines are still seen, while $K \neq 0$ lines disappear. This can be understood in terms of Coriolis coupling between the $14^1 \, 1^2$ state and other vibrational states within S_1 and a subsequent nonradiative process. This coupling might be the explanation for the drastic onset of line broadening in C_6H_6 at an excess energy of 3000 cm^{-1}, "channel three". The line broadening is then due to a different process than that responsible for the population lifetime of S_1.

Introduction

It is a well-known phenomenon that only the lowest excited singlet state of gas-phase polyatomic molecules shows sharp structure whereas the higher singlet states become diffuse. High-resolution one-photon spectra have revealed that this rule applies also for the prototype molecule benzene. There has, however, been found for this molecule a further limitation of the range of sharp spectra. One-photon spectra (Doppler-limited) show an onset of the diffuseness even in the S_1 system at an excess energy of 3000 cm^{-1}.[1] This onset of diffuseness coincides with a break off of fluorescence from the S_1 state[2] and was therefore interpreted as the onset of a novel radiationless channel in the molecule, "channel three". There has been some discussion about the possible origin of this radiationless process during the past decade, but no reasonable explanation about the nature of this "channel three" has been found, so far.

In a recent work[3] we have shown by measurements of fluorescence that the breakoff of fluorescence is less sharp than the onset of diffuseness found in ref 1. The fastest kinetic rates are two orders of magnitude smaller (10^{10} s^{-1}) than the rates (10^{12} s^{-1})[1] obtained from the line width measurements. This discrepancy led us to the conclusion that "channel three" responsible for the line broadening must be viewed as a process which does not affect the population of S_1, but rather must be a coupling within S_1. Line widths here just measure a process different from population lifetimes.

It was decided to attempt to measure highly resolved spectra which allow for the resolution of single rotational lines near this "channel three" region. Typical Doppler-limited high-resolution spectra only display the rotational band envelope.[4] Higher resolution is expected to yield quantitative results on the broadening which could give insight into the nature of the process.

An attempt in this direction recently has been performed by Aron et al.[5] in a supersonic jet experiment. Their resolution was strongly limited by the frequency width (2–3

GHz) of the laser and by the method of detection which was multiphoton ionization.[6] Still they were able to detect a single rotational line due to the cooling characteristics of the jet;[7] however, broadening could only be detected when it substantially exceeds the laser line width. At this level of line broadening (3 GHz), the unknown process is already so strong that any specific characteristic of the process necessary for its identification is smeared out. As we shall see later on for its identification it is extremely useful to observe not only one single rotational line but many of them. For this the freezing of rotational lines in a jet is not the method of choice.

The resolution of many rotational lines of a polyatomic molecule is possible with the method of Doppler-free two-photon absorption. Recent work in our group in the ambient benzene gas at room temperature has demonstrated that the rotational line structure in the electronic spectrum of a large molecule like C_6H_6 can be fully resolved.[8] In addition, using pulsed amplification of single-mode cw laser light power levels of 30 kW with a frequency width of 100 MHz have been achieved which enabled us to measure weak molecular absorption bands.[9] With this setup we are able to obtain highly (rotationally) resolved excitation spectra of the weakly fluorescing vibronic bands in the "channel three" region of benzene. It will be shown that the high-resolution technique provides the key information for the identification of the nature of the broadening process.

Experimental Section

The scheme of our experimental setup has been published elsewhere.[9] Briefly, the light of a single-mode cw ring laser (Coherent 699) is amplified in a two-stage dye amplifier setup. The amplifier cells are pumped with a N_2 laser (Molectron UV 1000) with a peak power of 600 kW. Coumarin 485 in dioxan is used as the amplifying dye at the wavelength of 4819 Å. The characteristics of the amplified laser pulses are as follows: 30 kW peak power (amplification of 3×10^5), frequency width 100 MHz (Fourier limited), pulse length 5 ns. The laser beam is focused with an achromatic lens ($f = 16$ cm) into the fluorescence cell containing benzene vapor at a pressure

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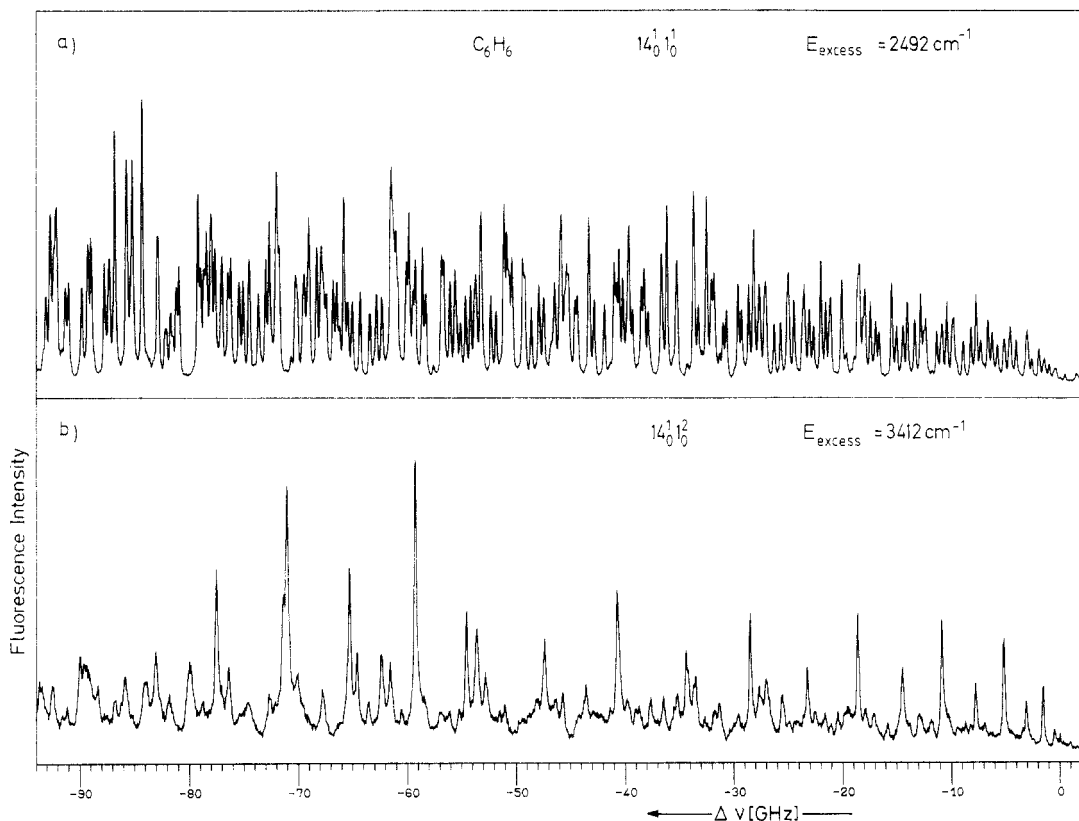
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Figure 1. Doppler-free two-photon fluorescence excitation spectra of C_6H_6: (a) part of the Q-branch of the $14_0^1 \, 1_0^1$ band at an excess energy of 2492 cm^{-1}; (b) corresponding part of the $14_0^1 \, 1_0^2$ band at 3412 cm^{-1}. Note the much lower number of lines in the $14_0^1 \, 1_0^2$ band.

of 4 torr. The laser beam is then refocused with a confocal mirror ($r = 16$ cm) so that both foci completely overlap (see Figure 1 in ref 9). Doppler-broadened two-photon absorption is suppressed by using countercircularly polarized light so that the observed spectrum is governed by the isotropic parts of the two-photon absorption tensor.[10,11] For this polarization condition the Doppler-broadened background is found to be negligibly small.

The emitted fluorescence has a double-exponential decay; the long component recently has been shown to be fluorescence from the thermalized level with a lifetime of about 70 ns, the short component has been identified as the direct fluorescence from the excited rovibronic level.[3] The fluorecence is integrated with a boxcar integrator (PAR 162); the digitized integrated signal is transferred to a DCS data processing system. Then it is processed as described in our recent work.[9]

Results and Discussion

Two-photon spectra of C_6H_6 measured as described in the previous section are shown in Figure 1, a and b. Figure 1a represents the $14_0^1 \, 1_0^1$ two-photon spectrum at 40 577-cm^{-1} two-photon energy in countercircularly polarized light. In the S_1 state in addition to the two-photon inducing mode ν_{14} (1570 cm^{-1}) one quantum of the totally symmetric C–C stretch mode ν_1 (921 cm^{-1}) is excited. Therefore, the excess energy of the final rotationless pure vibrational state in S_1 is 2492 cm^{-1}, about 500 cm^{-1} *below* the onset of "channel three". Due to the polarization of the photons the isotropic Q-branch ($\Delta J = 0$) dominates the spectrum of the totally symmetric $A_{1g} \leftarrow A_{1g}$ two-photon transition ($\Delta K = 0$[12]). Nearly no Doppler-broadened background

is observed in the spectrum. This rotational spectrum is very similar to that of the fundamental 14_0^1 vibronic band with slightly changed rotational constants[8,9] due to the additional quantum of the vibration ν_1. About 40% of the observed lines represent single rotational transitions.
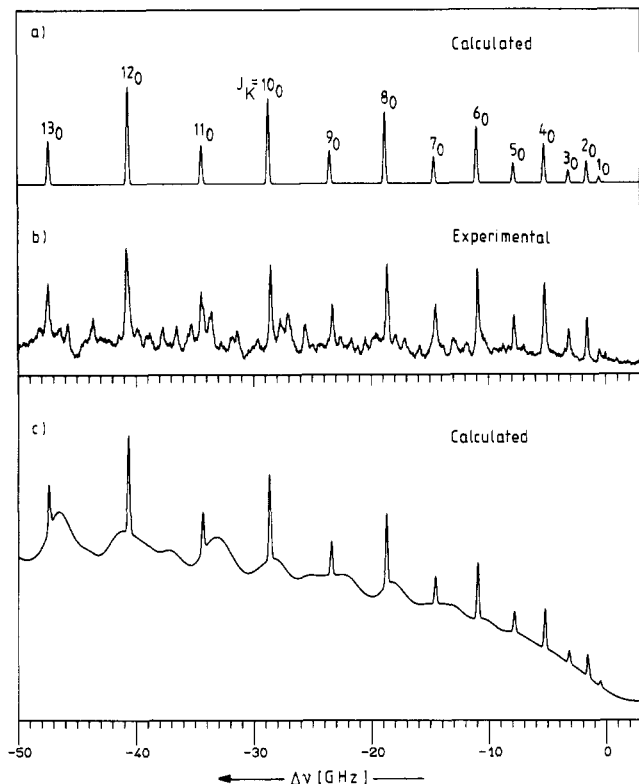
In Figure 1b the measured spectrum of the $14_0^1 \, 1_0^2$ vibronic band at 41 498 cm^{-1} is shown. Due to one further excited quantum of ν_1 the excess energy of the final rotationless state is 3412 cm^{-1}, about 400 cm^{-1} above the onset of "channel three". Even at first sight a striking discrepancy between both spectra is seen. Most of the many rotational lines present in the $14_0^1 \, 1_0^1$ band (Figure 1a) have disappeared in the $14_0^1 \, 1_0^2$ band (Figure 1b). Only a few sharp lines are left. These lines have a half-width of about 200 MHz which roughly corresponds to the resolution of the exciting laser light. The first wavenumber of the $14_0^1 \, 1_0^2$ spectrum very much resembles the spectrum of a diatomic molecule with no K structure. A closer inspection indeed shows that in this range of the spectrum only $K = 0$ lines appear. This is indicated by the frequency position of the lines and the striking alternating intensity of subsequent lines. This alternating intensity is due to the different statistical weights predicted to be 7 for $K = 0$ and J even and 3 for $K = 0$ and J odd in C_6H_6.[13] For a direct check of the intensity ratio, one has to consider the Boltzmann factor as well as the M degeneracy of the lines which together lead to an overall increase of line intensity with increasing J in the observed spectral range. This is demonstrated in Figure 2a. Here the calculated spectrum of the $K = 0$ lines up to $J = 13$ is shown. The value of the rotational constant $B_v = 0.18108$ cm^{-1} for this calculation was found from the frequency position of the $K = 0$ lines up to $J = 14$. It is smaller by 0.000 14 cm^{-1} than the

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Figure 2. (a) Calculated spectrum of a totally symmetric two-photon transition showing only $K = 0$ lines. (b) Corresponding part of the measured spectrum of the $14_0^1\ 1_0^2$ band shown in Figure 1b. (c) Calculated spectrum showing sharp $K = 0$ lines (210 MHz fwhm) on top of a background caused by the many broadened (3 GHz fwhm) $K \neq 0$ lines.

corresponding constant B_v of the $14_0^1\ 1_0^1$ band. This is a reasonable value since the quadratically averaged bond lengths in the molecule are somewhat increased when an additional quantum of ν_1 is excited.

There is an excellent agreement found for the calculated (Figure 2a) and the measured spectrum (Figure 2b) in the line positions as well as in the typical alternating intensity ratio of the rotational lines. This is a strong argument for our assignment. Further away from the vibronic band origin the $K = 0$ lines begin to die out (Figure 1b). $K = 0$ lines can be identified up to $J = 16$. Then other strong lines appear which begin to resemble a $J = K$ structure at 100 GHz from the rotationless origin.

In order to check the influence of excess energy on the rotational structure we measured the $14_0^1\ 1_0^3$ vibronic band at an excess energy of 4330 cm^{-1}. No structure at all was found in our high-resolution spectrum with a resolution of 200 MHz. This is in line with the result of Aron et al.[5] who found a broadening of about 37 GHz for this vibronic band from jet measurements. Obviously, at this energy level the unknown process responsible for the line broadening has become so fast that every structure in the spectrum is smeared out and specific information can no longer be obtained.

At this point we have to bring to mind again that in this work we measure fluorescence excitation spectra rather than absorption spectra. It is clear that all rotational lines are present in the absorption spectrum (which cannot be measured) since the general structure (symmetric top) of the molecule has not changed during the absorption process. The lines may disappear for two possible reasons:

(a) The first reason would be the disappearance of fluorescence from those final states which are populated by the missing rovibronic transitions. A fast radiationless process may be responsible for this. These lines are then absent in the excitation spectrum.

(b) The transitions which cannot be found in the measured spectrum are simply broadened; fluorescence emission takes place, but the lines are broadened to a smooth background.

In order to rule out one of the possibilities we simulate case (b). The oscillator strength of all lines with $K \neq 0$ has been taken into account but the corresponding lines have been convoluted with a Lorentz distribution with fwhm of 3 GHz. The sum of all lines with $K \neq 0$ then gives rise to the strong background in Figure 2c on top of which the sharp $K = 0$ lines (210 MHz fwhm) are located. There is no similarity at all to the measured spectrum in Figure 2b. The background in the measured spectrum is only about 10% of the background in the simulated spectrum in Figure 2c. From this we may conclude that all final states with $K \neq 0$ have a fluorescence quantum yield which is only less than 10% of the fluorescence quantum yield of the $K = 0$ final states. This result makes clear that the strong decrease of the $14_0^1\ 1_0^2$ band (7%) compared to the 14_0^1 band (100%) which has been found in our previous low-resolution measurements[12] is not due to a homogeneous decrease of the total band but to a selective dilution of rotational lines within the band. Probably, the $K = 0$ lines do not change intensity whereas the $K \neq 0$ lines decreased by at least a factor of 10, on the average. This is an unexpected result which demonstrates the importance of rotationally resolved spectra.

Conclusion

From the results in the preceding section it is clear that a rotationally highly selective nonradiative process takes place in the $14^1\ 1^2$ vibronic state of C_6H_6 at an excess energy of 3412 cm^{-1}. In the low J range ($J \lesssim 16$) the nonradiative process for $K = 0$ states is weaker by at least one order of magnitude than for $K \neq 0$ states.

In molecular spectroscopy two processes are known to be strongly dependent on the rotation of the molecule. The first is the predissociation of the molecule. A lack of K structure has already been observed for the much smaller HCO molecule.[14] This has been interpreted as a strongly K-dependent predissociation. The benzene molecule, however, is known to show no photochemistry above $\lambda > 2000$ Å.[2] The very careful and sensitive experiments of Callomon et al.[1] do not show any predissociation in the region of "channel three". Therefore we may rule out this process.

The second process which has to be considered is Coriolis coupling. Coriolis coupling is known to be strongly dependent on J or K.[15] Since obviously $K = 0$ states are not affected in the spectrum, i.e., Coriolis coupling is not present for $K = 0$ states, the coupling of the excited vibration to other vibrations should be produced by a rotation around the figure (z) axis of the benzene molecule (R_z). in $K = 0$ states the molecule does not rotate around the z axis which is perpendicular to the molecular plane. Therefore $K = 0$ states do not show Coriolis coupling. This yields the symmetry condition for the vibrations which are coupled by Coriolis interaction.

$$\Gamma_{\nu_{14}} \times \Gamma_{\nu_x} \times \Gamma_{R_z} = a_{1g}$$

For benzene (D_{6h}) and for $\nu_{14}(b_{2u})$ we have $\Gamma_{\nu_x} = b_{1u}$, i.e., a coupling of the $14^1\ 1^2$ state via Coriolis interaction R_z is possible to vibrational states of b_{1u} symmetry. In order to estimate the strength of the Coriolis coupling it would

(14) G. Herzberg, "Molecular Spectra and Molecular Structure", Vol. III, Van Nostrand, Princeton, 1966, p 214.

(15) Reference 14, p 68 f.

be necessary to check whether there are vibrational states of b_{1u} symmetry close in resonance with the $14^1\,1^2$ state. This is done in a forthcoming paper.[16]

Even if we assume that there are states of suitable symmetry in resonance with the $14^1\,1^2$ state and efficient Coriolis coupling takes place this would only explain a broadening of the lines with $K \neq 0$ or a frequency shift. A still open question would be the complete disappearance of the lines which has to be produced by a nonradiative process leading to another nonradiating electronic state (e.g., S_0 or T_1). Hence, we conclude that Coriolis coupling is the primary process for the nonradiative process which then is responsible for the disappearance of the fluorescence from $K \neq 0$ states.

A tentative explanation would be that Coriolis coupling is the process which couples the optically excited modes to those modes which induce the nonradiative process, e.g., ic or isc. At first sight the strict symmetry selection rule seems to strongly restrict the types of modes which can be coupled, so that a communication of states[17] seems to be impossible. However, one has to bear in mind the high excess energy of the $14^1\,1^2$ state ($3412\ \mathrm{cm}^{-1}$). At this excess energy many states with b_{1u} symmetry exist, which are made up from the combination of several different vibrational states, particularly of low frequency. Hence, we expect that a coupling of the optically excited mode is particularly efficient to low-frequency modes and several quanta of these modes can be excited by the Coriolis interaction. The modes of lowest frequency in the $^1B_{2u}$ state of benzene are the ν_{16} ($237\ \mathrm{cm}^{-1}$, e_{2u}) and the ν_4 ($365\ \mathrm{cm}^{-1}$, b_{2g}), both out-of-plane modes. Out-of-plane modes are known to play an important role in nonradiative processes. Experiments by Spears and Rice[18] and by our group[19] have

shown that the decay rate of states increases strongly with the excited number of ν_{16} quanta. Recent theoretical work[20] predicts that the ν_4 mode should play an important role in the ic process since it is expected to be a good acceptor mode at $3400\text{-}\mathrm{cm}^{-1}$ excess energy.

We think that in our high-resolution experiments we have observed the transition from an isolated state situation ($K = 0$ states) to a communicating state ($K \neq 0$) situation within a single vibronic band. The communication of the states is produced by Coriolis coupling and leads in turn to a rapid nonradiative decay of the originally excited ($K \neq 0$) states, since it couples to those vibrations which strongly induce the radiationless process. Due to the characteristic features and the rotational selectivity of Coriolis interaction there is no Coriolis interaction for $K = 0$ states. Therefore these states ($K = 0$) do not undergo a radiationless process and lead to sharp rotational lines in the $14_0^1\,1_0^2$ spectrum.

The results of this experiment point to a clear photophysical process, namely, Coriolis coupling, which is responsible for initiating the photochemistry, i.e., here the communication of states which leads to the excitation of the crucial vibrational levels required for the subsequent radiationless process. Coriolis coupling then would be the process responsible for the previously observed broad line widths[1] in the spectra in the "channel three" regime. It is the physics of an intramolecular process which precedes lifetime decay. Such onsets of intramolecular energy randomization may have obvious further implications in reaction kinetics.

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