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HETEROGENEOUS PERTURBATIONS IN THE DOPPLER-FREE $S_1 \leftarrow S_0$ TWO-PHOTON SPECTRUM OF BENZENE: EVIDENCE FOR INTRASTATE COUPLING

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Rotational perturbations are identified in Doppler-free two-photon spectra of the 14^1_0 and $14^1_0 1^1_0$ vibronic bands in C_6H_6. Evidence is found that Coriolis coupling between some of the rotational levels of two distinct vibrational states within S_1 is the mechanism responsible. This coupling mechanism is thought to be responsible for irreversible intramolecular relaxation at higher excess energies and higher vibrational state densities.

1. Introduction

Recently it was noted that relaxation rates of benzene S_1 vibronic levels deduced from fluorescence yield measurements [1] differ from those deduced from higher-resolution band contour measurements [2]. This deviation might be explained by intramolecular vibrational relaxation (IVR) prior to electronic relaxation in this excess energy range.

Prior information on IVR at high vibrational excess energies was drawn from frequency-resolved emission spectra [3] (for a review, see ref. [4]) under ambient gas and cooled supersonic beam conditions, as well as from oscillatory (quantum beat) emission behaviour [5]. In none of these studies have single rovibronic states been populated. And indeed rotational effects in IVR were deemed to be of minor importance.

In a Doppler-free two-photon experiment we were, however, able to show [6,7], that the relaxation behaviour of benzene in the "channel three" region [2] (above 3000 cm^{-1} vibrational excess energy) is strongly dependent on the rotation of the molecule, leading even to the absence of many rotational lines in the fluorescence excitation spectrum. Indirect evidence of rotationally dependent relaxation has also recently been reported for the case of pyrimidine [8]. In benzene Coriolis coupling seems to be responsible for the absence of many rotational lines in the spectrum [6] as well as for an increase in the homogeneous linewidth with increasing rotational quantum numbers of the remaining lines, as seen in our ultra-highly resolved spectra ($\Delta\nu < 10$ MHz) [7]. It was concluded, that the observed features could be explained by IVR followed by a fast non-radiative electronic relaxation process [6,7].

In order to clarify the mechanism of the coupling responsible for IVR in more detail, it is significant to study not only the high excess energy range as has been done so far but also the range of low excess energies. At low excess energies the density of background states is expected to be so small that the coupling responsible for the relaxation process exists only for distinct molecular levels which are accidentally in resonance with perturbing background states. Therefore, an irreversible relaxation process does not exist for these states at low excess energies. This situation is well known as the "small molecule" limit and coupling results, for example, in heterogeneous perturbations of the spectrum rather than in a broadening of lines.

Perturbations have been extensively studied for small molecules consisting of only a few atoms (see, for example ref. [9]). However, for the case of larger polyatomic molecules they have so far not been observed since the rotational lines could not be resolved, due to Doppler broadening.

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Recently we demonstrated that with Doppler-free two-photon spectroscopy, the rotational structure of the electronic spectrum of benzene can be completely resolved [10]. The increased spectral resolution of the present work allows a detailed analysis of the spectrum and heterogeneous perturbations are found at relatively low excess energies in S_1. The matrix elements of the coupling process responsible for the heterogeneous perturbations are measured and the origin of the coupling process discussed.

2. Experimental

The apparatus used in this work is similar to that described previously [7]. Q-branch spectra were measured with a cw Kr^+-laser-pumped single-mode dye laser. The overall experimental resolution in this case is about 6 MHz. For the weak S branch we used a pulsed light source consisting of the cw dye-laser system and two nitrogen-laser-pumped amplifiers according to our previous work [11]. This provides the necessary high peak power, but with an increased frequency width of 170 MHz.

Doppler-free two-photon excitation spectra were measured by reflecting back the incident laser beam with a confocal mirror. A Doppler-free signal is obtained when the foci of both the incoming and reflected beam overlap in the fluorescence cell containing the benzene vapour under a pressure of 1.5 Torr. In order to reduce the background in the spectrum polarization of both the incoming and reflected light beams can be chosen either linear or circular by polarizers and a λ/4 delay plate. The frequency scale of the measured spectra is calibrated with a temperature-controlled interferometer with a free spectral range of 1.4962 GHz and a finesse of better than 50. Frequencies are accurate to about 50 MHz.

3. Results and discussion

The rotational structure of the Q branch of the totally symmetric ($\Delta K = 0$) 14^1_0 and $14^1_0 1^1_0$ two-photon bands in C_6H_6 have been measured over 150 GHz to the red of the rotational origin.

3.1. 14^1_0 band

In recent work we have shown that the spectrum of the 14^1_0 band can be well reproduced with a set of rotational constants $\Delta B = B'_v - B''_0$ and $\Delta C = C'_v - C''_0$ up to −70 GHz if a rotational defect is taken into account [10]. First discrepancies, which seem to be irregular at first sight are observed for several lines between −70 and −100 GHz. As an example two small portions of the spectrum in this frequency range are shown in fig. 1. In the lower part of the figure the spectrum is plotted as calculated from the best set of rotational constants found in a complete analysis of the band [12]. In the upper trace the corresponding part of the measured spectrum is shown. Comparison of the measured and calculated spectrum shows agreement for most of the lines. Only one line ($J'_{K'} = 21_{17}$ and $J'_{K'} = 22_{17}$) in each calculated part of the spectrum is not found at the expected position in the experimental spectrum. A closer inspection shows that in-

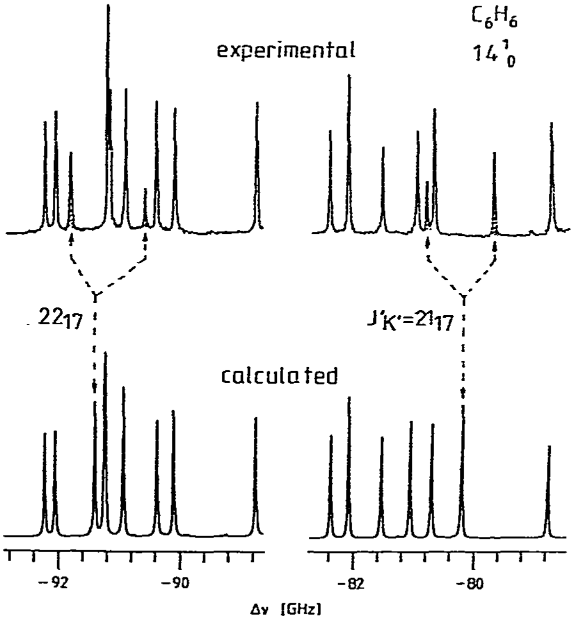

Fig. 1. Two parts of the Q branch of the 14^1_0 two-photon band of C_6H_6 under high resolution. Upper traces: measured Doppler-free spectra; lower traces: calculated spectra. Instead of the predicted peaks $J'_{K'} = 21_{17}$ and $J'_{K'} = 22_{17}$ two peaks appear shifted by about 0.5 GHz from the calculated position in each case.

stead of the single line two additional new lines appear which are shifted by about 500 MHz to both sides of the calculated position. The sum of the intensity of both lines is about 90% of the expected intensity of the missing lines. Between −40 and −130 GHz deviatins of experimental line positions from calculated positions as shown in fig. 1 are found for lines with $K' = 17$ and J' from 17 to 26. All other lines agree well with the calculated positions. In the left part of fig. 2 the residuals (observed minus calculated) of the frequency are plotted for four different K' values ($K' = 0, 3, 16$ and 17) and J' up to 25. If two components of a line are observed for one value of J' and K', the stronger one is marked as •, the weaker one as ○. For $K' = 0$, 3 and 16 the residuals are close to zero within experimental error. This means that the corresponding lines are found at the expected position. For $K' = 17$, however, the residuals shown in fig. 2 represent the typical shape of an avoided crossing curve with the crossing point between $J' = 21$ and $J' = 22$. The frequency distance of the split lines is 1.1 GHz at the crossing point, which corresponds to a coupling matrix element of $V \approx 0.55$ GHz.

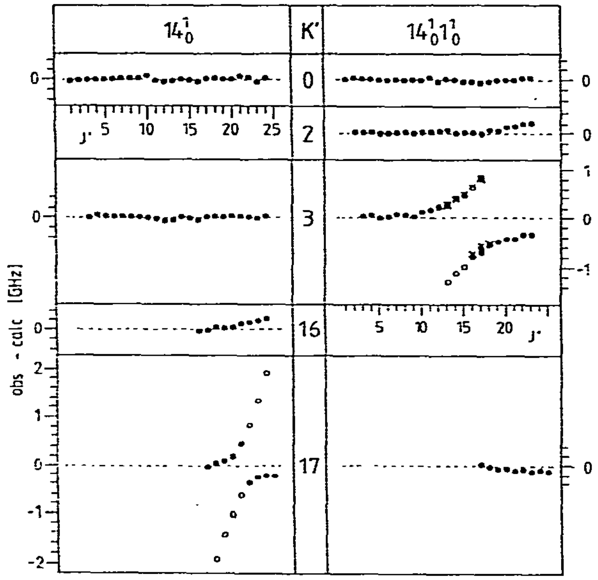

Fig. 2. Residuals (observed − calculated) of the frequencies of rotational lines in the $14^1{}_0$ and $14^1{}_0 1^1{}_0$ two-photon bands of C_6H_6 as a function of the final-state quantum number J' for several K'. If two components of a rotational line in the Q branch are observed the weaker is marked by ○, the stronger by •. Additional residuals found from the S branch of the $14^1{}_0 1^1{}_0$ band are marked by × (see fig. 3).

3.2. $14^1{}_0 1^1{}_0$ band

The situation in the Q-branch of this band is quite similar to the $14^1{}_0$ fundamental band: agreement of the calculated spectrum with the measured spectrum is obtained with a slightly different set of rotational constants (owing to the vibrational dependence of the rotational constants) [11,12] for nearly all lines up to −70 GHz from the rotational origin. Deviations from calculated line positions are found for lines with $K' = 3$ and J' between 10 and 23. In fig. 2 (right part) the residuals (observed minus calculated) of line frequencies are plotted for lines with $K' = 0, 2, 3$ and 17. For $K' = 2$ and 17 the residuals are close to zero, i.e. no perturbation is present for lines with these K' values. But for $K' = 3$ in the range $3 \leqslant J' \leqslant 23$ a rotational perturbation is found with the crossing point between $J' = 15$ and $J' = 16$ and a frequency splitting of 1.4 GHz which corresponds to a coupling matrix element $V \approx 0.7$ GHz. For this perturbation the second weak component again can be observed in the neighbourhood of the crossing point.

In order definitely to exclude the improbable possibility that the observed perturbations are due to a coupling within the ground state, two different checks have been performed.

(i) In the lower right-hand part of fig. 2 the residuals of all lines of the $14^1{}_0 1^1{}_0$ band with $K' = 17$ and J' from 17 to 25 are shown. In constrast to the left-hand part, where the residuals for the same rotational lines in the $14^1{}_0$ fundamental band are shown, no rotational perturbations are observed for these lines in the $14^1{}_0 1^1{}_0$ band. Both series of rotational lines have common ground states. It is clear that the observed perturbation of the $K' = 17$ lines is due to a coupling of rotational states with $K' = 17$ in the 14^1 vibronic state in S_1. The same procedure can be performed for the $K' = 3$ lines. Comparison of the residuals of the $K' = 3$ lines in the $14^1{}_0$ and $14^1{}_0 1^1{}_0$ band makes it clear that the coupling occurs in the final $14^1 1^1$ state.

(ii) In addition the origin of the perturbation of the $K' = 3$ lines in the $14^1{}_0 1^1{}_0$ band is checked in a somewhat different way. Rotational transitions with J' quantum numbers near the crossing point can be

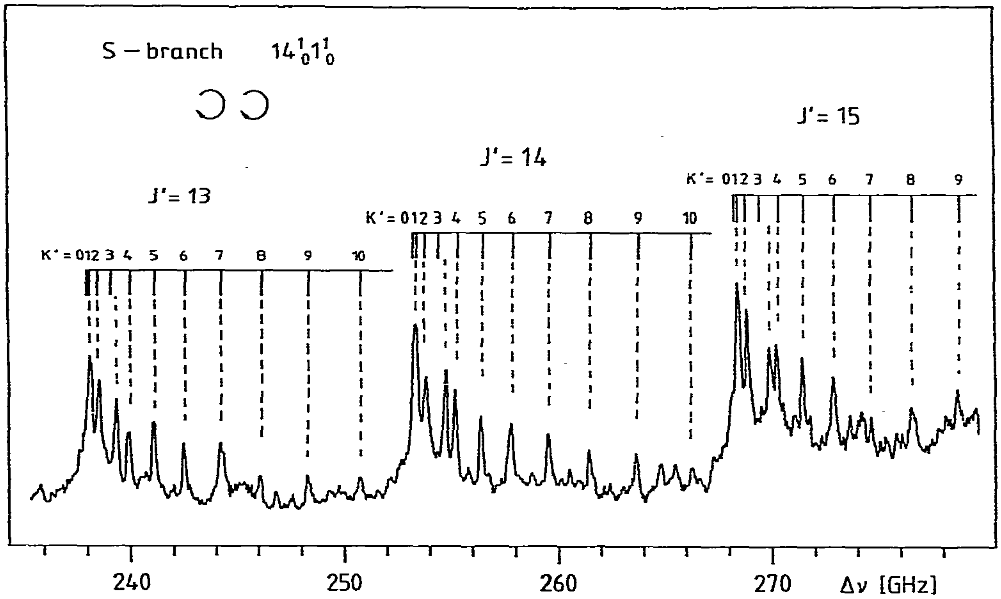

Fig. 3. Part of the S branch of the $14^1{}_0 1^1{}_0$ two-photon band of C_6H_6 measured with a pulsed apparatus [11] with both photons circularly polarized in the same sense. The measured K structure of three sub-bands with $J' = 13$, 14 and 15 is shown. The calculated K structure is marked at the top and it is seen that for each J' value the line with $K' = 3$ is shifted from the predicted position.

well identified in the S branch of the $14^1{}_0 1^1{}_0$ two-photon band. Since the ΔJ selection rules in the Q and S branch differ, transitions leading to the same final state start from a different ground-state level. Thus, a comparison of the crossing point position in the Q branch with that of the S branch enables us to decide whether the coupling occurs in the ground or the excited state. In fig. 3 the corresponding part of the S branch spectrum is shown. Due to the weak intensity of the S branch [13] the spectrum has been measured with the pulsed apparatus with a reduced spectral resolution. In this case the linewidth is 170 MHz.

It is immediately seen that the K structure of the transitions with $J' = 13$, 14 and 15 is not as regular as it should be if no perturbation were present. In this case the distance of neighbouring K lines should increase quadratically for a planar symmetric top [14] as is indicated above for each sub-band in fig. 3. The residuals found from the S branch are plotted in fig. 2 as a function of J' and marked by X. It is seen that the rotational perturbations in the Q branch and the S branch appear for the same final-state rotational state quantum numbers J', K' and it is clear that this perturbation is due to a coupling in the final state.

4. Discussion

The experimental results show that in the S_1 state of benzene selective coupling to some other "dark states" is present at low excess energies (1570 and 2492 cm^{-1}). Since perturbations are observed for a particular K' value ($K' = 17$ in $14^1{}_0$ and $K' = 3$ in $14^1{}_0 1^1{}_0$) and lines with neighbouring K' values do not reveal a perturbation (see $K' = 16$ of $14^1{}_0$ and $K' = 2$ of $14^1{}_0 1^1{}_0$ in fig. 2) we may exclude the selection rule $\Delta K = 0$ for the coupling process.

At this point the question about the nature of the coupled state has to be discussed. Does the coupling process take place between states within S_1 (intrastate) or is the coupled state from another electronic manifold (interstate)? Candidates for an interstate coupling are the $S_0(^1A_{1g})$, $T_1(^3B_{1u})$ and $T_2(^3E_{1u})$ states. S_0 and T_1 may immediately be excluded due to their very high density of states at an excess energy of about

40000 and 10000 cm^{-1}, respectively. It would be hard to understand how the observed extreme selectivity of the coupling process, which combines only two distinct states due to an accidental resonance, could take place in the quasi-continuum of S_0 and T_1 states. The third possibility for an interstate (spin–orbit) coupling, to the $T_2(^3E_{1u})$ state, has to be considered in more detail. The position of the T_2 state was found to be 36400 ± 200 cm^{-1} [15] and therefore the vibrational excess energy of a coupled state would be between 3000 and 4000 cm^{-1}. It is conceivable that for the density of states in this excess energy range, selective coupling to a single state is possible. However, it has to be taken into account that probably all vibrational levels in T_2 are broadened due to the strong vibronic coupling to the T_1 state [16]. The vibronic coupling to the T_1 state is expected to be strong due to the small energy gap between T_2 and T_1. If the coupling observed in our experiment were due to a spin–orbit interaction with a broadened vibrational level in the $^3E_{1u}$ state, a broadening of lines near the crossing point should be observed. The reason for this would be that at the crossing point both states are mixed and the broadened triplet state coupled in with 50% probability. If γ_s and γ_ℓ are the homogeneous collision-free linewidths of the zero-order singlet state and triplet state, respectively, at the crossing point the linewidth should be $(\gamma_s + \gamma_\ell)/2$ if the coupling matrix element $V \gg \gamma_\ell - \gamma_s$ (strong coupling limit) [17]. To check this, the measured homogeneous linewidths of the transitions, particularly near the crossing point, have been considered in more detail. Our experiments have been performed at a pressure of 1.5 Torr yielding a collisional broadening of 22.5 MHz for the collision-broadening parameter of 15 MHz/Torr found in our recent work [7]. Our measured value of 25 ± 3 MHz for the homogeneous linewidth is in good agreement with the expected value if the difference of 2.5 ± 3 MHz is attributed to the finite resolution of 6 MHz (Gaussian distribution) of our apparatus [7] as well as to the rather small relaxation linewidths (Lorentzian) of 1.3 (2.4) MHz typical for the 14^1 ($14^1 1^1$) two-photon state. This linewidth can be deduced from our previous lifetime measurements integrated over many rotational states in the 14^1 and $14^1 1^1$ vibronic state [18]. Within the experimental error of ±3 MHz no increase of the homogeneous relaxation linewidth is found at the crossing point where strong mixing occurs. From this result, it is concluded that the linewidth γ_ℓ of the zero-order coupled state does not differ very much from the linewidth γ_s of the zero-order excited state and the coupled state has the dynamic behaviour typical for an S_1 state in this excess energy range. From this result we may exclude that spin–orbit coupling to a vibronic state in T_2 is responsible for the observed rotational perturbations. An unambiguous identification of the coupled state would be possible by applying a magnetic field, thus checking whether the coupled state has a magnetic moment due to non-zero spin.

The only possibility left is then an intrastate coupling to other vibrational states within S_1 with the selection rule $\Delta J = 0$ and $\Delta K \neq 0$. Since $\Delta K \neq 0$, anharmonic mixing as the responsible coupling process is excluded. A possible coupling process which allows $\Delta K \neq 0$ is perpendicular Coriolis coupling [19] and we tentatively conclude that perpendicular Coriolis coupling to dark vibrational states within S_1 is responsible for the observed rotational perturbations (heterogeneous perturbation). This is an important result in view of our recent results on non-radiative processes in the "channel three" region at even higher excess energies [6,7]. There we have shown that Coriolis coupling is a significant primary process in intramolecular vibronic relaxation of S_1 benzene.

Next, we have to check whether vibrational states of proper symmetry are in the vicinity of the excited 14^1 and $14^1 1^1$ states. We have calculated the positions of combination states which contain the symmetry species $\Gamma_{\nu_x} = e_{2u}$ necessary for perpendicular Coriolis coupling $(R_{x,y})$ with the excited vibrational b_{2u} state in benzene (D_{6h}) $(\Gamma_{b_{2u}} \otimes \Gamma_{\nu_x} \otimes \Gamma_{R_{x,y}} \supset a_{1g})$.

Within ±100 cm^{-1} of the 14^1 vibrational origin we find 16 combination states with an e_{2u} symmetry component. The distance of the closest combination band has been calculated to be 7 cm^{-1}. It is, however, hard to decide on a particular combination band out of this ensemble due to the uncertainties of the vibrational frequencies. Errors of several 10 cm^{-1} have to be taken into account since several vibrational frequencies are not known from experiment and had to be calculated from the excited-state force field [20]. All combination states in the energy range under consideration contain at least 2 vibrational quanta, some of them up to 5. This means that only higher-order Coriolis coupling processes can mix the optically excited 14^1 and the dark states under consideration.

This is in qualitative agreement with the rather small value of the coupling matrix element of 0.55 GHz.

For the $14^1 1^1$ state at 2492 cm^{-1} excess energy, the density of states with an e_{2u} symmetry component increases drastically. Within ±20 cm^{-1} we find already 29 states each at least containing 3 and some even 7 vibrational quanta. Even though it is not possible to find and identify a particular state to be responsible for the observed coupling process, since the vibrational frequencies are too uncertain, it is seen that there exist several states with proper symmetry within the energy interval of some cm^{-1}. This remaining energy mismatch of the pure vibrational frequencies can then be compensated when rotations are excited due to the somewhat different rotational constants of the couple states and a $\Delta K \neq 0$ selection rule. In this way it is possible to compensate for some cm^{-1} and even more if $\Delta K > 1$ as could be the case in a higher-order coupling process.

5. Summary and conclusion

In this work a very high resolution spectrum of part of the $14^1{}_0$ and $14^1{}_0 1^1{}_0$ vibronic bands ($S_1 \leftarrow S_0$) of C_6H_6 has been measured. The very high resolution of $\nu/\Delta\nu \approx 5 \times 10^7$ has become available through Doppler-free two-photon spectroscopy. The analysis of the spectra reveals several heterogeneous perturbations. Two of them appearing at the lowest rotational energy in the $14^1{}_0$ ($E_{rot} = 57.6$ cm^{-1}) and $14^1{}_0 1^1{}_0$ ($E_{rot} = 48.8$ cm^{-1}) band are analyzed in detail. Coupling matrix elements V of about 0.55 and 0.7 GHz, respectively, are found. From the measured K dependence of the heterogeneous perturbations and the measured homogeneous linewidths near the crossing point, it is concluded that the interaction of two vibrational states within the S_1 electronic state coupled via perpendicular Coriolis coupling is observed. This result is in line with our recent results in the $14^1{}_0 1^2{}_0$ band at the higher excess energy of 3412 cm^{-1} [7]. There it has been found that the homogeneous linewidth of rotational lines is strongly dependent on K and J and Coriolis coupling (within S_1) plays an important role in the relaxation process.

In conclusion, it is now possible to investigate spectroscopic perturbations in larger polyatomic molecules as has been done in the past for much smaller molecules. This has become feasible due to the application of high-resolution Doppler-free two-photon absorption in molecular spectroscopy. Precise information about intrastate and interstate coupling mechanisms is of great importance for the understanding of the intramolecular relaxation process. Coupling between distinct vibrational states as observed in this work might be the precursor of the intramolecular vibrational relaxation process at small excess energies where even in a larger polyatomic molecule the density of vibrational states is rather low and not sufficient for an irreversible relaxation process.

A detailed analysis of the benzene spectrum at higher excess energy is in progress, with the aim to clarify how the increasing density of states influences the intrastate coupling and the intramolecular relaxation behaviour. Doppler-free two-photon spectroscopy here becomes crucial for the analysis of the molecular dynamics, since it allows the resolution of single rotational lines.

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References

[1] L. Wunsch, H.J. Neusser and E.W. Schlag, Z. Naturforsch. 36a (1981) 1340.
[2] J.H. Callomon, J.E. Parkin and R. Lopez-Delgado, Chem. Phys. Letters 13 (1972) 125.
[3] H.F. Kemper and M. Stockburger, J. Chem. Phys. 53 (1970) 268.
[4] C.S. Parmenter, Faraday Discussions Chem. Soc. 75 (1983) 7.
[5] P.M. Felker and A.H. Zewail, Chem. Phys. Letters 102 (1983) 113.
[6] E. Riedle, H.J. Neusser and E.W. Schlag, J. Phys. Chem. 86 (1982) 4847.
[7] E. Riedle and H.J. Neusser, J. Chem. Phys. 80 (1984) 4686.
[8] B.E. Forch, K.T. Chen, H. Saigusa and E.C. Lim, J. Phys. Chem. 87 (1983) 2280.

[9] D.J. Clouthier, D.C. Moule, D.A. Ramsay and F.W. Birss, Can. J. Phys. 60 (1982) 1212.
[10] E. Riedle, H.J. Neusser and E.W. Schlag, J. Chem. Phys. 75 (1981) 4231.
[11] E. Riedle, R. Moder and H.J. Neusser, Opt. Commun. 43 (1982) 388.
[12] E. Riedle and H.J. Neusser, in preparation.
[13] L. Wunsch, F. Metz, H.J. Neusser and E.W. Schlag, J. Chem. Phys. 66 (1977) 386.
[14] G. Herzberg, Molecular spectra and molecular structure, Vol. 3 (Van Nostrand, Princeton, 1966).
[15] S.D. Colson and E.R. Bernstein, J. Chem. Phys. 43 (1965) 2661;
C.S. Parmenter, Advan. Chem. Phys. 22 (1972) 365.
[16] G.W. Robinson, J. Chem. Phys. 47 (1967) 1967.
[17] W. Dietz, Doctoral Thesis, Technische Universität München (1983).
[18] L. Wunsch, H.J. Neusser and E.W. Schlag, Chem. Phys. Letters 32 (1975) 210.
[19] I.M. Mills, Pure Appl. Chem. 11 (1965) 325.
[20] M. Robey and E.W. Schlag, J. Chem. Phys. 67 (1977) 2775;
R.P. Rava, J.G. Philis, K. Krogh-Jespersen and L. Goodman, J. Chem. Phys. 79 (1983) 4664.