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Sub-Doppler Spectroscopy of Benzene in the 'Channel-three' Region

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In addition to an increased accuracy in the determination of structural parameters sub-Doppler spectroscopy of large molecules is shown to render valuable information about intramolecular processes and relaxation mechanisms. As an example we have measured the Doppler-free rotationally resolved two-photon spectrum of two vibronic bands of C_6H_6, $14^1_0 1^1_0$ and $14^1_0 1^2_0$. Compared with the $14^1_0 1^1_0$ band ($E_{\text{excess}} = 2492$ cm^{-1}) a drastically reduced number of sharp lines is observed in the $14^1_0 1^2_0$ band ($E_{\text{excess}} = 3412$ 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 non-radiative 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 from that responsible for the population lifetime of S_1.

1. INTRODUCTION

High-resolution spectroscopy of molecules renders precise new information on the energy levels of the molecule and in some cases information about intramolecular processes. Assuming that an assignment of the transitions is possible, the accuracy of the determination of the energy levels is only limited by the resolution obtainable in the experiment.

To extract information about intramolecular processes from the spectrum which is complementary to decay-time measurements,[1-4] exact knowledge of the linewidth of individual transitions is desirable. In the gas phase typical decay rates are of the order of $k = 10^8$ s^{-1}, corresponding to a linewidth given by $k/2\pi c = 0.0005$ cm^{-1} according to the uncertainty principle. The resolution obtainable in the electronic spectrum of gas-phase molecules is limited by Doppler broadening, which is typically 0.06 cm^{-1} (for benzene and 40 000 cm^{-1} transition energy). This shows that for this example only a very crude upper limit of the rates can be found by conventional Doppler-limited spectroscopy.

On the other hand rates of 10^{10} s^{-1} produce a linewidth of 0.05 cm^{-1}, which is far greater than the average spacing of rotational lines within a vibrational band. Therefore in this case it is not possible to observe the lineshape of a single transition in the molecule.

To gain exact information it is therefore clear that Doppler-free spectra have to be recorded. This was recently accomplished by us for the first time for a large polyatomic molecule, benzene, using the method of Doppler-free two-photon spectroscopy.[5] These experiments were performed using a c.w. dye laser and an Ar^+ laser, both lasers having extremely narrow bandwidths. Owing to the relatively modest intensities of the lasers only the strongest bands could be observed, while weaker bands of great interest could not be detected. This problem was overcome by setting up a continuously scanable pulsed laser system with a Fourier-transform limited bandwidth of 0.003 cm^{-1}.[6] This resolution proved sufficient to resolve most of the individual rotational lines of a vibronic band for a molecule as large as benzene. The sensitivity of the set-up is now sufficient to record all bands of interest in molecules such as benzene. From the results reported in this paper it becomes clear that the method of Doppler-free two-photon spectroscopy combined with the sensitivity of the pulsed system provides a large improvement in accuracy. This improvement is sufficient to allow observation of new effects in intramolecular processes originating from defined quantum states of the molecules under consideration.

2. THE " CHANNEL-THREE " PROBLEM

It is a general rule that only the lowest excited singlet state in a gas-phase polyatomic molecule shows sharp structure. For the prototype molecule benzene high-resolution (Doppler-limited) one-photon spectra revealed [7] that even in the S_1 state this is only true up to a vibrational excess energy of ca. 3000 cm^{-1}. At the same point of the spectrum a sudden break-off of fluorescence is also observed.[8] The process responsible for this phenomenon was termed " channel three " owing to this unexplained behaviour, and has been subject to discussions and experiments during the past decade. Similar behaviour has been seen in other molecules,[9] suggesting that " channel three " is a general property of many aromatic molecules.

In recent work by our group [10] it was shown that the break-off of fluorescence is less sharp than the onset of diffuseness found in ref. (7), i.e. diffuseness starts suddenly near 3000 cm^{-1}, whereas rate constants continue to shorten with energy in a near-normal fashion. Pressure-dependent quantum-yield measurements for the $14^1_0 1^n_0$ bands lead to rates which are two orders of magnitude smaller than the rates calculated from the line-broadenings in the diffuse bands given in ref. (7). Both sets of values are summarized in fig. 1. The explanation found for this discrepancy was that in the line-broadening experiment the general dynamic behaviour of the specific vibronic state populated is observed, while in the quantum-yield measurements and in decay-time measurements the population lifetime of the vibronic level is monitored. Neither of the two experiments, however, measured the linewidth of a single rovibronic state nor its lifetime. Rotational-state-selectivity might further complicate this picture. Aron et al.[11] attempted to avoid this by measuring the linewidth of single states in a supersonic-jet experiment. The resolution (2–3 GHz) of their laser system limited them to the observation of bands far above the onset of " channel three". Bands at the onset are the ones most likely to clarify the nature of " channel three", since they might show a transitional character between the unperturbed and broadened spectra, and promise to give a quantitative measurement of the process which is occurring. The results shown later make it clear that the rotational structure of the observed bands should be resolved in order to provide a complete understanding. With the laser system mentioned above we are now able to perform this task looking at the spectra of individual rotational states in the region near the onset of " channel three".

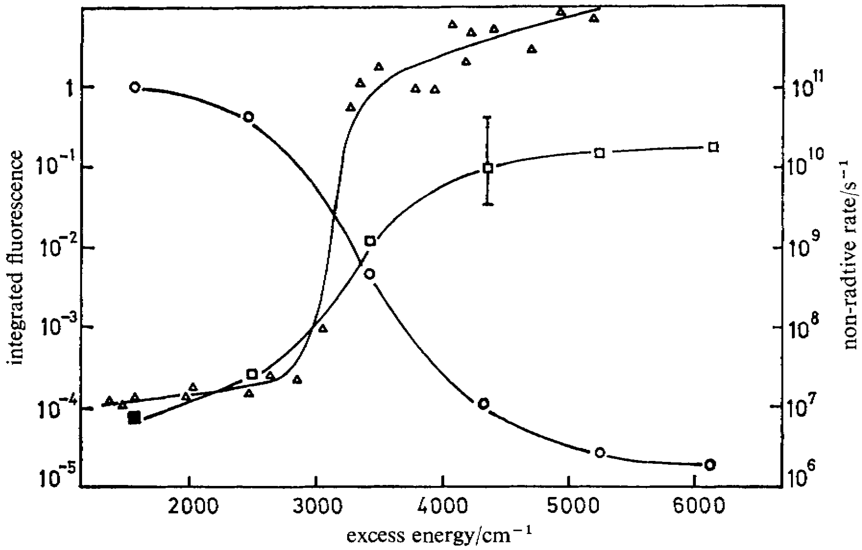

Fig. 1. Non-radiative rates for various vibrational levels in S_1 of benzene as a function of excess energy. The values have been obtained in different experiments from: △, direct time-resolved decay measurements of states at low excess energies ($\leqslant 3000$ cm^{-1}) excited by one-photon [2] and two-photon absorption; [4] △, linewidth measurements of one-photon transitions to states at high excess energies ($\geqslant 3000$ cm^{-1}); [7] □, as estimated in ref. (10) from quantum-yield measurements for the $14^1 1^n$ states. These quantum-yield values were calculated from the values of the integrated fluorescence (○) [from ref. (10)].

3. EXPERIMENTAL SET-UP

Pulsed dye lasers of the Hänsch type [12] or similar design are in practice limited to a resolution of 0.05 cm^{-1} even if an intracavity etalon is used. An external confocal etalon inserted between the oscillator and amplifier [13] will improve this value; however, the resulting system is hard to scan continuously over an extended frequency range, as is needed in molecular spectroscopy. A design which delivers the desired pulsed light of near Fourier-transform-limited bandwidth has been reported by Salour.[14] We have adopted this design with some modifications as demanded by our needs.[6] In short it consists of a c.w. dye laser whose output is amplified in two stages pumped by the light of a N_2 laser. A scheme of our experimental set-up is shown in fig. 2. The c.w. dye laser used is a Coherent CR 699–21 ring laser operating with C 102 around 490 nm and an output power of at least 100 mW. It is pumped by the violet light of a CR 3000 K UV Kr^+ laser. The wavelength of the c.w. light is monitored with a Burleigh WA–20 wavemeter to an accuracy of 0.03 cm^{-1}. The c.w. system is optically decoupled from the amplifier system by a direct-vision prism. Owing to the relatively high input power we are able to manage with two amplifier stages pumped by a UV 1000 N_2 laser with a total power of 700 kW. To suppress amplified spontaneous emission from the dye cells we insert narrow-band (f.w.h.m.-30 Å) interference filters after each stage. These allow easy tuning over wide ranges, as needed in our experiment, by angle tuning. With C 481 in dioxan as amplifying dye we obtain up to 100 kW of 5 ns light pulses with an almost Fourier-transform-limited bandwidth of 100 MHz. The total power of broadband-amplified spontaneous emission is smaller by more than a factor of 10. The pulsed laser light is focused into a fluorescence cell containing 4 Torr of benzene (C_6H_6). The beam is then reflected with a confocal mirror and the two foci are carefully overlapped. To suppress the Doppler-broadened background caused by the absorption of two photons from one direction we insert two $\lambda/4$ plates as shown. These are adjusted such that the laser beams are counter-clockwise circularly polarized (as seen in the reference system of the molecule).

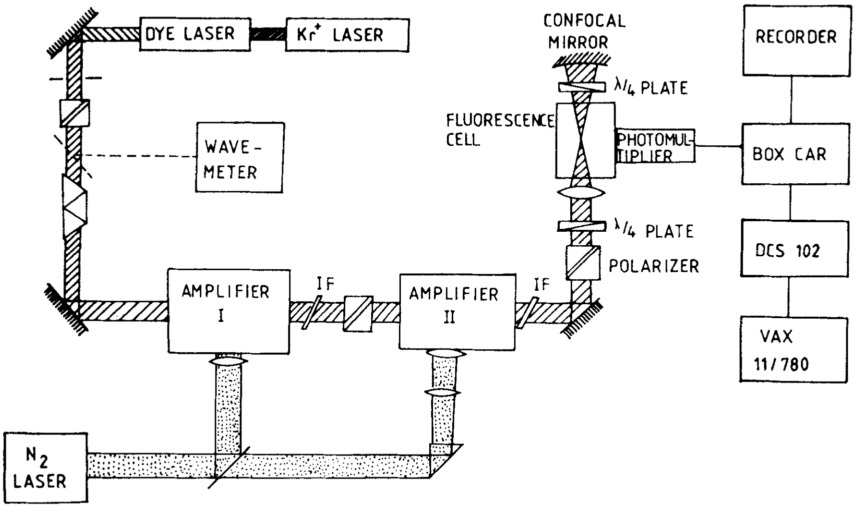

Fig. 2. Experimental set-up for recording Doppler-free two-photon electronic spectra of C_6H_6. The single-mode c.w. dye laser output is amplified in two stages pumped by the pulsed light of the N_2 laser. The resulting light pulses are used for the excitation of the molecules [from ref. (6)].

The effect of this procedure can be understood in terms of the different tensorial contributions to the two-photon absorption if the correct geometrical factors are considered.[15,16] The u.v. fluorescence of the molecules is observed with a solar-blind (9 mm UG5 Schott filters) 56 DUVP photomultiplier. The signal is integrated with a PAR 162 box-car integrator and digitized in a DCS 102 microprocessor system. Then it is transferred to a VAX 11/780 computer where it can be printed with suitable scaling factors and evaluated.

4. RESULTS

With the set-up described in the previous section we have measured the Doppler-free two-photon spectrum of part of the isotropic Q-branch ($\Delta J = 0$) of the $14^1_0 1^1_0$ band (2492 cm^{-1} excess energy) and the $14^1_0 1^2_0$ band (3472 cm^{-1}),[17] as shown in fig. 3. In the $14^1_0 1^1_0$ band ca. 40% of the observed lines represent single rotational transitions. As before in the 14^1_0 band [5] we observe a slight negative inertial defect, but the rotational structure agrees very well with rigid-symmetric-rotor calculations. The vibronic energy of 2492 cm^{-1} is ca. 500 cm^{-1} below the onset of " channel three", so this good behaviour is not unexpected. The $14^1_0 1^2_0$ band at 3412 cm^{-1} shows a strikingly different structure. Most of the rotational lines present in the $14^1_0 1^1_0$ band have disappeared in this band. Only a few sharp lines are left. These lines have a half-width of ca. 220 MHz, which roughly corresponds to the frequency resolution of our system. In order to check the influence of excess energy on the rotational structure we also recorded part of the $14^1_0 1^3_0$ band at 4330 cm^{-1} excess energy. With our high-resolution set-up we did not notice any significant structure even though ample signal strength was found at the position of the spectrum assigned to this transition by Wunsch et al.[18] This result agrees very well with the linewidth of 37 GHz [11] found previously for the $14^1_0 1^3_0$ band in the jet experiment. Obviously at this high excess energy the process responsible for " channel three " is so fast that no more rotational structure is left.

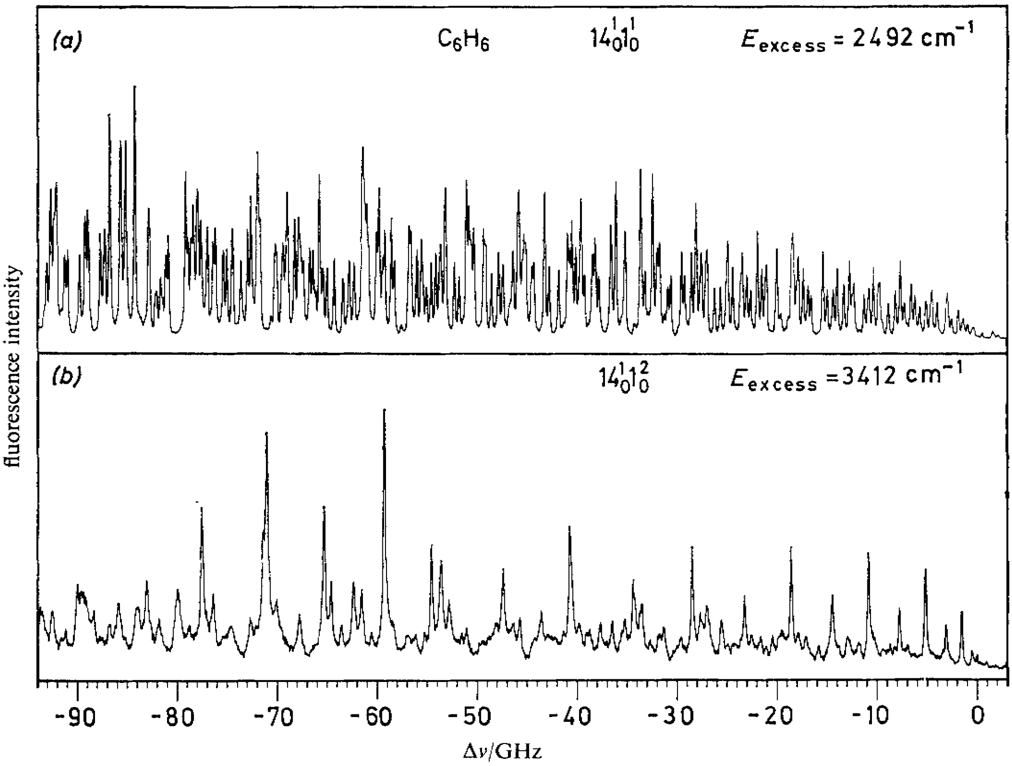

Fig. 3. Doppler-free two-photon fluorescence excitation spectra of C_6H_6: (*a*) part of the Q-branch of the $14^1_0 1^1_0$ band at an excess energy of 2492 cm^{-1}; (*b*) corresponding part of the $14^1_0 1^2_0$ band at 3412 cm^{-1} [from ref. (17)].

5. DISCUSSION

In order to understand the rotational structure of the $14^1_0 1^2_0$ band and to reveal the nature of the process responsible for it, the sharp lines in the spectrum have to be identified. The lines between −50 and 0 GHz show a striking variation in intensity of roughly 2 : 1, as can be seen in detail in fig. 4(*b*). This could be explained by the 7 : 3 intensity ratio predicted for the $K = 0$ lines of the $14^1_0 1^2_0$ band owing to the changing statistical weights between even and odd J values.[19] To check this assumption the exact positions of these lines were determined to an accuracy of better than 50 MHz and compared with the ones predicted by rigid-symmetric-rotor calculations. The value of $B'_v = 0.081\,08$ cm^{-1} used was found from a least-squares fit to the measured positions up to $J = 14$. It is smaller by 0.000 14 cm^{-1} than the corresponding B'_v value found for the $14^1_0 1^1_0$ band,[6] a reasonable change owing to the added quantum of ν_1. The deviation of the calculated and measured positions was in all cases significantly less than the linewidth. The calculated spectrum of the $K = 0$ lines is given in fig. 4(*a*) for comparison. This excellent agreement of the line positions together with the alternating intensity is then taken as sufficient evidence for the proposed assignment as $K = 0$ lines. Further away from the origin the dominance of the $K = 0$ lines disappears and possibly a $K = J$ structure appears.

To understand the dominant role of the $K = 0$ lines in this spectrum, which are barely seen in the 14^1_0 band [5] or the $14^1_0 1^1_0$ band [6] owing to their low intensity, one must bear in mind that we are measuring fluorescence excitation spectra. In the absorption spectrum, which is difficult to measure for two-photon transitions, all lines should show up according to symmetric-top theory regardless of any processes occurring after absorption. However, if as in our experiment the fluorescence of the excited states is monitored, three distinct possibilities have to be considered: (*a*) The transitions not seen in the spectrum lead to states which undergo a fast radiationless decay. Therefore the corresponding lines are absent in our fluorescence excitation spectrum. (*b*) The missing transitions are very much broadened but fluorescence is seen. They therefore contribute to the spectrum as broadband background. (*c*) The transitions are shifted away by several cm^{-1} to another part of the spectrum. The reason for this shift would be spectroscopic perturbations such as Fermi resonance and Coriolis coupling, well known from the spectra of smaller molecules.

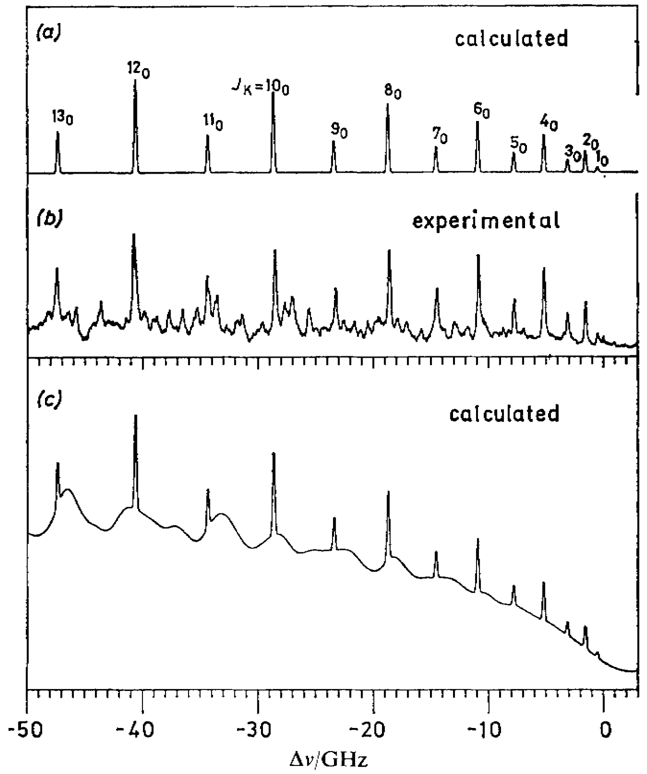

Fig. 4. (*a*) Calculated spectrum of a totally symmetric two-photon transition showing only $K = 0$ lines. (*b*) Corresponding part of the measured spectrum of the $14^1_0 1^2_0$ band shown in fig. 3(*b*). (*c*) Calculated spectrum showing sharp $K = 0$ lines (210 MHz f.w.h.m.) on top of a background caused by the many broadened (3 GHz f.w.h.m.) $K \neq 0$ lines [from ref. (17)].

The last point can be ruled out. From a test of the rovibronic spectrum at different points of the rotational contour it is clear that there is a decreased number of lines throughout the rotational band. If the rotational lines were shifted from one part of the band to another, the density of lines would be increased at this other part of the band.

To clarify the remaining questions a symmetric-rotor calculation was performed and the contributions from lines with $K \neq 0$ were convoluted with a Lorentzian distribution of 3 GHz f.w.h.m. while the $K = 0$ lines were convoluted with a Gaussian distribution of 210 MHz f.w.h.m. The resulting spectrum is shown in fig. 4(*c*). It does not resemble the measured spectrum of fig. 4(*b*). The broadened background of the calculated spectrum is too high by at least a factor of 10. Keeping in mind that Wunsch et al.[18] had found a strong decrease of the intensity of the $14^1_0 1^2_0$ band as compared with the $14^1_0 1^1_0$ band of 7 : 100, this can be consistently explained as a strong decrease of the fluorescence quantum yield of the $K \neq 0$ states while the $K = 0$ states are unchanged. Possibility (*a*) above therefore has to be preferred as a conclusion. Clearly this result demonstrates that it does not suffice to observe states of extremely low J and K values as in a supersonic-jet experiment to gain a full understanding of the intramolecular processes in large molecules.

6. CONCLUSION

The results of the last section point to a rotationally highly selective non-radiative process that takes place in the $14^1 1^2$ state at an excess energy of 3412 cm^{-1}. It is stronger by at least a factor of 10 for most $K \neq 0$ states compared with the $K = 0$ states in the regime $J < 16$.

There are two obvious processes in molecular spectroscopy that show a strong rotational dependence. The first process is predissociation; however, the benzene molecule is known to show no photochemistry below 50 000 cm^{-1}.[8] Also the experiments of Callomon et al.[7] did not show any evidence of predissociation in the region of " channel three". These arguments leave Coriolis coupling. There can be Coriolis coupling of the excited state to other vibrational states due to rotation around either the z-axis or the x,y-axes of the molecule. Both couplings are known to be strongly dependent on K.[20] The coupling sought after should not be effective for $K = 0$ states, as was discussed above, and therefore only rotation about the z-axis is a possible coupling mechanism. The symmetry selection rule

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

renders for benzene (D_{6h}) and for $\nu_{14}(b_{2u})$ $\Gamma_{\nu_x} = b_{1u}$ for the coupled vibration ν_x. This symmetry is given for the normal modes ν_{12} and ν_{13} in benzene, all possible progressions of these and all possible combination bands of this overall symmetry. We calculated possible vibrational combinations fulfilling the symmetry condition and having an energy close to the $14^1 1^2$ state. A detailed discussion will appear elsewhere.[21]

Even though this calculation showed that there might be states sufficiently close to the $14^1 1^2$ state, this Coriolis coupling would only explain the broadening of lines with $K \neq 0$ or a frequency shift. However, the strong disappearance of the fluorescence remains to be explained. This would require a subsequent non-radiative process after the redistribution of energy caused by the Coriolis coupling.

Inspection of the calculated vibrational combinations shows that most of them contain quanta of out-of-plane modes. These modes are just the ones known to play an important role in non-radiative processes. Previous experiments [2,4] have shown the ν_{16} mode to be of particular importance and the ν_4 mode is predicted [22] to play an important role in the IC process since it is expected to be a good acceptor mode at 3400 cm^{-1} excess energy. Either of these two modes is present in most of the combinations calculated. For these reasons it is reasonable to suppose that the energy deposited in the $14^1 1^2$ state is redistributed by Coriolis coupling to other modes within the S_1 manifold followed by a fast non-radiative process. Hence we would expect to observe a transition from an isolated state ($K = 0$) to a communicating state ($K \neq 0$) in our high-resolution experiment.

The linewidth of 220 MHz of the transitions observed gives a very much improved estimate on the single-state linewidth. It is still mainly determined by the resolution of our set-up; however, this upper limit gives a lower limit to the expected lifetime of 0.7 ns, which is in good agreement with earlier measurements.[10] Also the corresponding rate of 1.4×10^9 s^{-1} is reasonable for this high excess energy. A further improvement in the spectral resolution and lifetime measurements of single rotational states should very soon yield the exact values needed for an understanding of the nature of " channel three". The rotational dependence of these properties is already seen to play an important role in this analysis. These experiments are presently in progress in our laboratory.

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