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Collisional dephasing of the Na 13*d*-13*f* transition using the Ramsey method of separated rf fields

T. F. Gallagher and W. E. Cooke

Molecular Physics Laboratory, Stanford Research Institute International, Menlo Park, California 94025

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The collisional dephasing of the Na 13*d*-13*f* transition by Ne and CO has been investigated using the Ramsey method of separated radio-frequency fields. Upper limits for the dephasing cross sections are determined which are far smaller than the geometric size of the excited Na atoms. This leads to the conclusion that the separation of the potential cruves of the Na 13*d*-*X* and 13*f*-*X* states is nearly constant as a function of internuclear separation.

I. INTRODUCTION

Although highly excited Rydberg atoms have large geometrical cross sections, their effective cross sections for collision processes vary from orders of magnitude smaller than the geometrical cross sections to cross sections somewhat larger than the geometrical cross sections; the range suggesting that different interactions are responsible for the collision processes. For example, Gounand *et al.*[1] have shown that quenching of excited Rb atoms by rare-gas atoms has a cross section of ~10 Å^2 even when the geometrical cross section of the excited Rb atom is ~10^4 Å^2. Similarly, Kocher and Smith[2] have observed deflections of a beam of Rydberg Li atoms in collisions with rare-gas atoms. The observed cross sections for deflection of the beam are ~100 Å^2, far smaller than the geometrical cross sections of the Rydberg atoms, and the deflections are attributed to Li$^+$-rare-gas scattering, a conclusion which is physically appealing on the basis of momentum transfer.

Perhaps the most dramatic collisional effects involving Rydberg atoms are those which exhibit large cross sections, such as the collisional l mixing of the excited Na d states in which the Na d states are collisionally mixed with the nearly degenerate higher l states of the same n. For rare-gas collision partners this has been shown to have a cross section nearly as large as the geometrical cross section of the excited Na atom.[3] Theoretical calculations indicate that the interaction of the rare-gas atom with the Na Rydberg electron is responsible for the process.[4,5] Recently, Flusberg *et al.*[6] have used a photon-echo technique to measure the cross sections for the collisional dephasing of the Na $3p$-ns and $3p$-nd transitions by rare-gas collision partners for $n=4-7$. They found the cross sections to be slightly larger than the geometrical cross sections of the excited Na atoms. However, it was not clear what mechanism lead to the large cross sections.

Since the Na d-state collisional l mixing cross sections for $n>10$ are smaller than the geometrical size of the Rydberg atom, it seemed to us quite possible that relatively gentle collisions producing small relative phase changes between nd an nf states without inducing a transition could have much larger cross sections, especially in light of the experiments of Flusberg *et al.* Accordingly, we undertook the study reported here of the collisional dephasing of the Na 13*d*-13*f* transition by Ne and CO in the hope that the information obtained would lead to new insights into Rydberg-atom collisions. We used the Ramsey method of temporally separated radio frequency (rf) fields, and, to our knowledge, this is the first use of the Ramsey method of separated rf fields to directly investigate collision processes.

II. GENERAL APPROACH

To understand the basis of the method, it is useful to review the Ramsey rf resonance method. Since a detailed description is given by Ramsey,[7] we shall only outline here the method as we have applied it to the Na d and f states.[8]

Although the experiment is done in a vapor cell, the temporal resolution of the laser excitation, rf transition, and flourescence detection makes the experiment analogous to a molecular beam experiment. In the experiment the atoms are intially excited to the 13*d* state by pulsed lasers and are then subjected to two pulses of an rf field, each of length t, and separated by a time τ. The first rf pulse drives the atoms halfway from the 13*d* state to the 13*f* state and the second rf pulse drives them the rest of the way. After the second rf pulse we detect the fluorescence from those atoms which have undergone the d to f transition. In practice, this method leads to a resonance which has an envelope of width $1/t$ and an interference pattern with maxima separated by $1/2\tau$.

An example of such a Ramsey resonance pattern is shown in Fig. 2(a).

For application to the study of collision processes, an important aspect of the Ramsey method of separated rf fields is that in the time τ between the two rf pulses the atoms are in a coherent superposition of the d and f states. As discussed in detail by Ramsey, changes in the phase of the two rf fields, or equivalently, changes in the phase between the d and f states during the time τ between the two rf pulses produce frequency shifts in the interference pattern. The effect of each phase-changing collision is to shift the interference pattern slightly, the magnitude of the shift determined by the details of the collision, such as the collision velocity and impact parameter. Clearly, for an ensemble of atoms the average result of collisions producing random shifts in the interference pattern would be to wash out the interference pattern, leaving only the envelope of the resonance. An important aspect of the technique is that by delaying our observation of the fluorescence, we only observe those atoms which have not undergone state-changing collisions, in particular collisional l mixing. Thus the Ramsey method is ideally suited for the study of phase-changing collisions in cases where there has been no change of state, only a change in phase.

Since measurements of pressure shifts and broadenings have been done for many years, it is of interest to compare other approaches to the method used here. In the measurements of rare-gas induced pressure shifts of higher alkali p states carried out by Amaldi and Segre,[9] high pressures (~1 atm) of rare gas were used with the result that many rare-gas atoms were in the orbit of the Rydberg electron at all times, so each alkali atom experienced the same pressure shift. In our experiments the rare-gas pressure is very low so that the dispersion in the phase shifts due to differing impact parameters and collision velocities is roughly equal to the average magnitude of the phase shift, even if all the phase shifts have the same sign. As Fermi[10] pointed out, however, phase shifts are not necessarily in the same direction because there are two interactions which are important.

It is also possible to look for pressure shifts and broadenings of the Na 13d-13f transition without using the separated rf fields, and in fact we have done so and have failed to observe any shifts or broadenings of a $\frac{1}{2}$-MHz (FWHM) linewidth resonance at Ne and CO pressures up to the pressures where the resonance was unobservable. In principle and in practice, such an experiment gives the same information as the use of the separated rf fields. However, the Ramsey method, since it provides clear maxima and minima, better enables us to discern broadening without detailed curve fitting.

III. EXPERIMENTAL DETAILS

The experimental approach is a synthesis of those described in detail in Refs. 3 and 8, so we shall only outline it here. We excite Na atoms to the $13d_{3/2}$ state using two pulsed tunable dye lasers as shown in Fig. 1. The Na is contained in a Pyrex cell which is heated to a temperature of 160 °C. The microwave power at 39.4 GHz is directed into the cell by a microwave horn a few centimeters away, and we detect the infrared 13f-3d and 3d-3p fluorescence from atoms which have undergone the 39.4-GHz transition from the $13d_{3/2}$ to the $13f_{5/2}$ state. The microwave power is applied in two pulses of 0.1-μs duration separated by 0.6 μs, and we sample the fluorescence for a 0.5-μs period just after the second rf pulse. As the rf frequency is swept through the $13d_{3/2}$ - $13d_{5/2}$ frequency, we observe the d-f resonance as an increase in the infrared fluorescence. For the study of collisional dephasing, foreign gas is added to the cell, and its effect on the d-f resonance is observed as a function of the foreign gas pressure. The pressure range we are able to study is limited by the collisional l mixing which transfers atoms from the 13d state to the higher l states. This increases the infrared background and, more importantly, equilibrates the d and higher l state populations, making the detection of the transition impossible. Thus, it is not

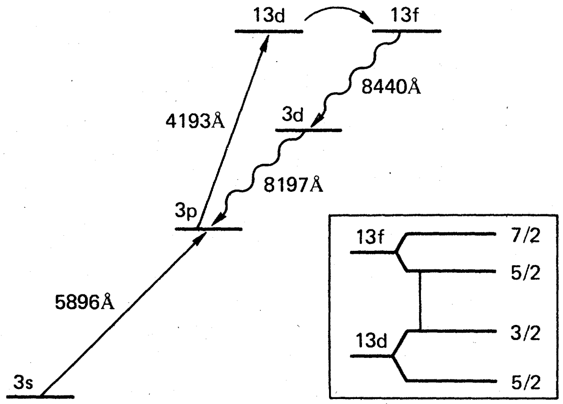

FIG. 1. Energy levels for the experiment. The upward straight arrows indicate the two laser pumping steps. The downward wavy arrows indicate the observed fluorescent decays and the curved arrow indicates the microwave d-f transition. The inset shows the 13d and 13f levels, the vertical line indicating the $13d_{3/2}$ - $13f_{5/2}$ transition under study.

possible to observe phase-changing collisions if the cross sections are smaller than the l-mixing cross sections. In such a case it is only possible to set an upper bound on the phase-changing cross sections.

IV. OBSERVATIONS

The effects of both Ne and CO were studied. Ne was chosen because its l-mixing cross section is two orders of magnitude smaller than the geometric size of the Na $n=13$ atom, allowing us to look for very small dephasing cross sections. CO was chosen because it is a polar molecule which we originally thought would lead to a large dephasing cross section. In both cases, though, we observed the same effect. As the foreign gas pressure was increased, the interference pattern did not disappear more rapidly than the envelope of the resonance; that is, the relative depth of the modulation did not change. For example, the resonances observed with 0 and 7.2 mTorr of Ne are shown in Fig. 2. Although the signal with 7.2 mTorr of Ne is noticeably noisier, it is evident that the depth of the modulation of the interference pattern has not decreased relative to the amplitude of the envelope of the resonance. In Fig. 3 we show a plot of the ratio R of the modulation depth of the interference pattern to the height of the envelope of the resonance as a function of Ne pressure. At neon pressures >20 mTorr we were unable to observe the resonance due to collisional l mixing. Similar results were obtained in CO at pressures of up to 2 mTorr. The pressure range that can be investigated with CO is lower due to its larger l-mixing cross sections.[11] The observation that, to an accuracy of 20%, there was no decline in the relative depth of the modulation of the Ramsey interference pattern suggests that the phase-changing cross sections are at least a factor of 5 smaller than the l-mixing cross sections. The upper bounds on the dephasing cross sections for both Ne and CO are given in Table I, as well as the average l-mixing cross sections.

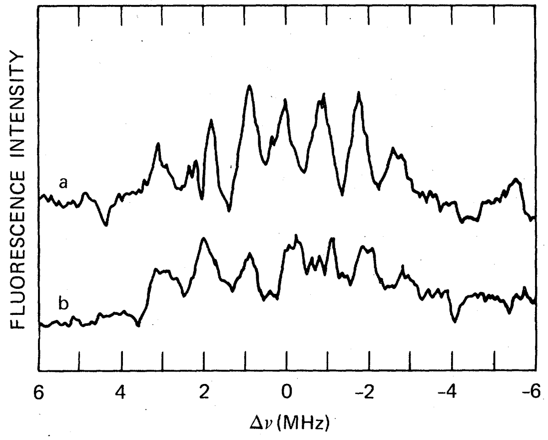

FIG. 2. Na $13d_{3/2}$-$13f_{5/2}$ resonances observed using the Ramsey method of separated rf fields. (a) Resonance observed with no Ne. (b) Resonance observed with 7.2 mTorr of Ne in the Na cell.

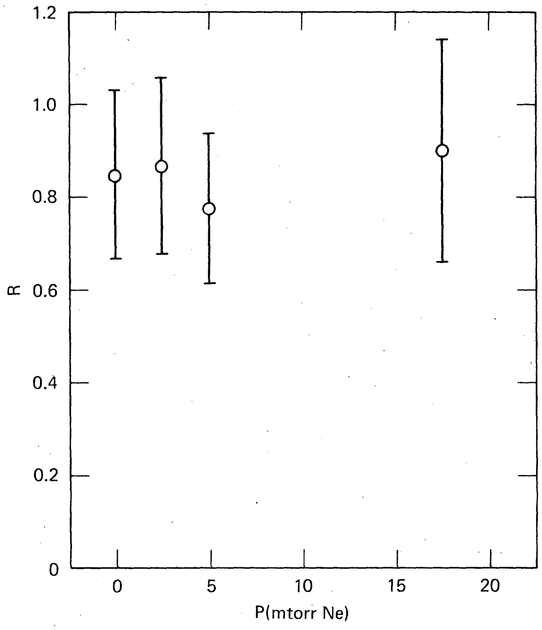

FIG. 3. Plot of the ratio R of the amplitude of the modulation depth to the amplitude of the resonance envelope vs Ne pressure.

At first glance it may seem impossible to obtain phase-changing cross sections smaller than the l-mixing cross sections. Recall though that because of the experimental approach we are observing only those atoms which remain in the d and f states. Thus, only the part of the l mixing which changes the relative d-f populations is important in these experiments and sets a lower limit on the observed dephasing cross sections. As we shall outline in Sec. V, only a fraction of

TABLE I. Geometrical, l-mixing, and phase-changing collision cross sections for Na $13d$.

	Geometric (Å^3)	l mixing (Å^2)	d-f transition phase changing (Å^2)
Ne	2.4×10^3	425[a]	<85
CO	2.4×10^3	2.44×10^3[b]	<500

[a] See Ref. 12.

[b] See Ref. 11.

the l-mixing cross section should be effective in producing observable dephasing in this experiment, so that an observed dephasing cross section which is 20% of the l-mixing cross section is not impossible, or as we shall see, unreasonable.

V. DISCUSSION

Let us consider for a moment the possible origins of collisional dephasing of the Na 13d-13f transition. First, dephasing can be caused by real, collisionally induced transitions from 13d to 13f or by preferential collisional depopulation of either the d or f states (to the higher l states). Second, there can be adiabatic relative energy shifts of the two levels during a collision leading to relative phase shifts between the two levels. The total dephasing cross section is given by the sum of these two effects.

Consider first the contribution of real state-changing collisions, which obviously disrupt the phase. What is the cross section for inducing the 13d-13f transition (or vice versa)? From previous experiments[12] which show that there are no strong Δl selection rules for l mixing, a reasonable estimate is σ/n, where σ is the l-mixing cross section. For $n=13$, this is then $\sigma/13$. Consider now the difference in collision cross sections for transitions of the 13d and 13f states to higher l states. Previously[12] we have shown that the difference in the 13d and 13f l-mixing cross sections for Ne is (with substantial uncertainties) ~30% of the average of the two, which should lead to a dephasing cross section of ~30%, of the average of the two l-mixing cross sections. For Ne, the l-mixing cross section given in Table I is the average of the 13d and 13f l-mixing cross sections. Together these two state-changing processes should lead to a dephasing cross section which is 35% of the l-mixing cross section, which is higher than what we observe as an upper limit for the dephasing cross section. Thus, we are led to the conclusions that probably the difference in the d and f l-mixing cross sections are not quite 30% and that there must be very little dephasing due to energy differences in the adiabatic Na 13d-Ne and Na 13f-Ne potential curves. This seems at first a remarkable conclusion. To decide if it is reasonable, let us examine how phase changes occur due to this mechanism.

In the time τ between the two rf pulses the total phase difference between the 13d and 13f states is simply

$$\phi=\int_0^\tau \Delta E\,dt\,, \tag{1}$$

where ΔE is the energy difference between the 13d and 13f states. In the absence of any foreign gas, or more generally any collisions, ΔE is a constant, the d-f interval. If foreign gas is added to the cell, then ΔE becomes a function of the internuclear separation between the excited Na atom and the foreign gas. Thus the total phase difference depends strongly on the difference $\Delta E(r)$ between the Na 13d-X and Na 13f-X potential curves as a function of r. If $\Delta E(r)$ is a constant for all r and equal to $\Delta E(\infty)$, the Na d-f separation, this mechanism will not produce collisional phase changes even if both levels are considerably shifted. However, if $\Delta E(r)$ varies from $\Delta E(\infty)$, then it will be possible to observe the randomizing effects of phase-changing collisions as described in Sec. II.

Our observations imply that the Na 13d-Ne and Na 13f-Ne potential curves are approximately equally spaced at all internuclear separations. More precisely we can say that the phase shift is ≤ 1 rad for impact parameters down to ~5 Å for Ne and 12 Å for CO. If we use a typical collision velocity of 5×10^4 cm/s and require that a phase shift of 1 rad occur, Eq. (1) implies that the energy difference $\Delta E(r)$ between the Na 13d-X and Na 13f-X potentials is given by

$$\left|\Delta E_\infty-\Delta E(r)\ (\mathrm{cm}^{-1})\right|\leq 4/r\ (\text{Å}) \tag{2}$$

for values of r greater than 4 Å for Ne and 12 Å for CO. There are two values of r which are particularly interesting, the radius of the Rydberg-electrons orbit, and the observed upper limit for the effective impact parameters for dephasing. At the radius of the $n=13$ orbit, 85 Å, Eq. (2) implies that the separation of the two curves must be within 0.05 cm^{-1} of the separation at $r=\infty$, 1.3 cm^{-1}. For Ne an impact parameter ≥ 5 Å apparently does not produce dephasing, therefore applying Eq. (2) at this value of r, the difference of the separation of the potential curves from the $r=\infty$ value, must be less than 0.8 cm^{-1}.

Let us consider our conclusion in light of the two interactions which are responsible for the energy dependence of the potential curves—the interaction of the Na$^+$ core with the perturber, and the interaction of the Rydberg electron with the perturber. These interactions are those considered by Fermi in his explanation of the pressure shifts observed by Amaldi and Segre. The Na$^+$ core polarizes the perturbing atoms within the Rydberg-electron's orbit; that is, the rare-gas atoms form a dielectric, always leading to a red shift of the spectral lines. The importance of the second effect, the e-rare-gas interaction, was first pointed out by Fermi, who noted that it could lead to red or blue shifts depending on the sign of the scattering length of the rare-gas atom. In Fig. 4 we show the potential curves of the Na-Ne system for the highly excited Na 13*d* and 13*f* states as well as the 3*p* state. It is interesting to estimate the energy shifts due to these interactions to see if Eq. (2) is satisfied. To estimate the energy shifts caused by these interactions, let us assume that the wave function of a state n is localized in shell of radius n^2 and thickness n. Using this model for the wave function and following Hickman,[5] we can estimate the energy shift due to the short-range ($\sim 3a_0$) Rydberg-electron–Ne interaction to be $\sim L/4\pi n^5$, where L is the scattering length of the Ne (or other collision partner) for $n^2 - \frac{1}{2}n < r < n^2 + \frac{1}{2}n$, and zero otherwise. Since the spatial extent of the *nd* and *nf* states is very nearly identical, we expect that the two potential curves would be displaced by identical small amounts, $\sim 10^{-2}$ cm^{-1} at $r = 85$ Å due to this interaction. Thus the difference is not enough to produce dephasing. Now let us consider the Na$^+$-Ne interaction. If the Ne is within the shell of the valence electron's orbit, it is clear that it experiences a net electric field due to the Na$^+$ core which polarizes the Ne leading to an energy shift of $-\alpha/2r^4$ for $r < n^2 - \frac{1}{2}n$ and zero for $r > n^2 - \frac{1}{2}n$. Again, since the spatial extent of the 13*d* and 13*f* wave functions is identical we expect that the 13*d* and 13*f* potential curves would both be displaced ~ 5 cm^{-1} at $r = 5$ Å, so that it is clear that the potentials will be within 0.8 cm^{-1} of each other as required by Eq. (2). Thus we find that quantitative estimates of the energy shifts indicate that the 13*d* and 13*f* potentials should remain roughly equidistant, in accord with the conclusions drawn from the experiments.

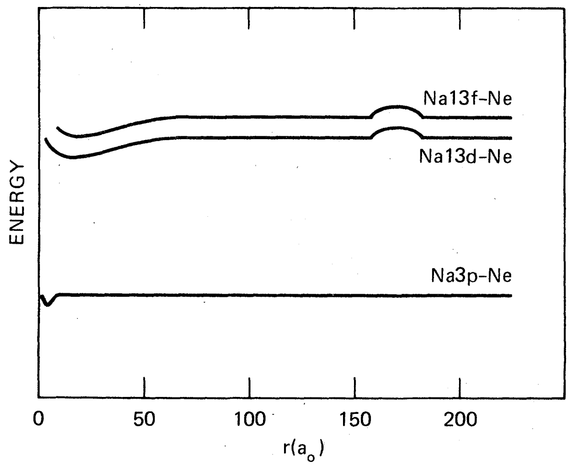

FIG. 4. Qualitative potential curves for the Na-Ne system. The well in the Rydberg states for $r < 75a_0$ is due to the Na$^+$-Ne interaction and the hump at $\sim 170a_0$ is due to the *e*-Ne interaction. The depth of the well and hump and displacement of the 13*d* and 13*f* states is exaggerated.

Now let us consider the case studied by Flusberg *et al.*, transitions from the Na 3*p* state to higher *ns* and *nd* states. They reported dephasing cross sections much larger than the geometrical size of the *ns* and *nd* states, and it is of some interest to consider the possible origin of such large dephasing cross sections. If we consider first the possibility of dephasing by real collisional transitions, we conclude that it is unlikely. The largest state-changing collisional effect is the depopulation of the *nd* states by collisional *l* mixing, and the cross sections are an order of magnitude smaller than the reported dephasing cross sections. For the Na 7*d* state, for example, the Ar *l*-mixing cross section[3] is 1500 Å^2 while the 3*p*-7*d* dephasing cross section[6] is 12 000 Å^2. Consequently, we are led to the conclusion that the dephasing must be due to the adiabatic energy shifts of the two potential curves, an effect that is negligible for the 13*d*-13*f* transition. From the dephasing of the 3*p*-7*d* transition we can estimate the difference in the Na 3*p*-Ar and Na 7*d*-Ar potentials. If we again use a velocity of 5×10^4 cm/s, require a relative phase of 1 rad, and use an input parameter of 50 Å, we find that

$$\Delta E_\infty - \Delta E(50\ \text{Å}) \approx 0.3\ \text{cm}^{-1}, \tag{3}$$

almost an order of magnitude larger than the corresponding value for the 13*d*-13*f* transition. This is not unexpected, though, since the spatial extent of the 3*p* and 7*d* states are very different, and they will be affected differently by the presence of a rare-gas atom at any internuclear separation because of both above mentioned interactions. As a consequence, their potential curves would not be parallel as a function of r and dephasing will occur because of the accumulated phase difference during a collision. Making an estimate of the Na$^+$-Ar polarization interaction at $r = 50$ Å we find that the Na-7*d* potential is depressed by 4×10^{-3} cm^{-1}, whereas using the Ar scattering length of $-1.70a_0$(Ref. 13) we find the shift due to the Rydberg-electron – Ar interaction to be -0.4 cm^{-1} above the minimum required by Eq. (3). Thus it appears that it is the latter interaction which is responsible for the dephasing.

It is interesting to note that for states of the same n, and therefore of the same spatial extent, dephasing is due mainly to real collisions, and hardly at all to differences in the adiabatic potential curves. However, for states of different n, the dephasing cross sections are larger, and are not due to real collisions, but to the differences in variation of the adiabatic potential curves with r.

The experiments have shown clearly that the energy separation of the potentials for the Na 13*d*-Ne and Na 13*f*-Ne systems is essentially constant as a function of internuclear separation, even though both potentials may experience considerably larger changes in energy. An important consequence of this result is the confirmation of the method used by Olson[4] to calculate Na l-mixing cross sections. In his calculations he assumed that the interaction between the d and f curves causing the collision took place over an extended region of r where the curves were parallel and close to each other rather than at a well localized curve crossing.

Although we are confident that it is the difference in the adiabatic potential curves which leads to the dephasing of the Na $3p \rightarrow ns$ and $3p \rightarrow nd$ transitions, the suggestion that it is the Rydberg-electron – rare-gas interaction which is primarily responsible is less certain. The Rydberg – rare-gas model presented here suggests that the dephasing cross sections should increase as the geometrical size of the Rydberg atom until $n \sim 10$ for Ar and then decrease as the decreasing density of the Rydberg electron reduces the shift of the *nd* potential curve. We might note that roughly similar behavior is observed for the Na *nd* l-mixing cross sections which are attributed to the same Rydberg-electron – rare-gas interaction. Using the model of the Na^+ – rare-gas interaction we estimate that the dephasing cross sections due to the Na^+-Ar interactions should be ~ 300 Å^2 independent of n for $n > 5$. Once the radius of the valence electron's orbit is larger than the maximum parameter which produces a phase change of making the orbit larger has no effect on the Na^+ – rare-gas dephasing cross section. Consequently one can imagine that at high enough n eventually the Na^+ – rare-gas interaction will dominate. In any event it should be straightforward to investigate these hypotheses by extending the 3*p*-*ns* and 3*p*-*nd* photon echo experiments to higher states.

Finally, we would like to emphasize the potential of the Ramsey separated rf field resonance method for collision studies. It is a simple, yet powerful, way to derive information about interaction potentials.

Note added in proof. It has recently been brought to our attention that spatially separated rf fields have been used to study relaxation in a molecular beam of NH_3 and OCS.[14]

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