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Cross-revival of molecular wave packets

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We predict that vibration-rotation coupling in diatomic molecules will lead to cross-revivals of vibrational wave packets—provided lifetime effects and collisions can be eliminated. Analytical conditions for full cross-revivals of systems governed by the minimal Hamiltonian exhibiting rotation-vibration coupling are found and the influence of higher-order cross terms is studied. Finally, generality of the phenomenon of molecular cross-revival is investigated by doing numerical calculations for several molecular potentials and temperatures. For expansion-cooled molecules strong cross-revivals are obtained in all cases. In the particular example of cold Li_2 in the $A\,{}^1\Sigma_u^+$ state nearly complete cross-revivals are observed. These cross-revivals survive thermal averaging and reach at an initial temperature of 900 K an amplitude which is close to half the beat amplitude at zero time delay. The ''rotational cooling'' mechanism facilitating this, by reducing the effective rotational temperature of the wave packet, is explained in terms of the molecular rotational constants and laser wavelength bandwidth.

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I. INTRODUCTION

Ever since the first studies of wave packets in diatomic molecules, it has been customary to try to separate vibrational and rotational contributions to coherent transients. At the same time it has been noted that this separation is inadequate and that the influence of vibration-rotation coupling has to be considered both in ''pure'' vibrational transients, i.e., recorded in magic-angle configuration, and ''pure'' rotational transients, as measured as the time-dependent anisotropy parameter. This coupling leads at low temperatures to complicated shapes of rotational transients and to narrowing of vibrational beat structures at elevated temperatures [1]. Nevertheless, revivals of the decayed vibrational transients exhibiting the classical vibrational period were observed [2], as well as fractional revivals [3,4], for which the vibrational beating takes place at some overtone of the classical frequency.

The rapid initial decay of the vibrational revival structure due to the broad rotational population distributions obtained under thermal conditions has lead many authors to treat the rotational degree of freedom classically. The summation over rotational states then simplifies greatly by reducing to an integration which often can be done analytically. An example of the utility of this approach was recently presented by Ermoshin, Kazansky, and Engel [5]. The price for this simplification is to give up the quantum nature of the rotation, which yields an unphysical monotonous decay of the vibrational revival amplitude.

Now, wave packets in free molecules left unperturbed by collisions stay coherent virtually indefinitely (we ignore for the moment possible lifetime effects), which means that one could expect a long-term revival of the vibrational beat amplitude, as the rotational energies causing the vibrational dephasing are quantized. Recent theoretical studies have, for example, shown that a complete revival of wave packets depending on two independent quantum variables is possible in general [6,7] and for atomic Rydberg wave packets in particular [8]. These results were obtained for the lowest-order generic Hamiltonian capable of displaying such cross-revivals, i.e., a Hamiltonian being quadratic in both quantum numbers and having a cross-term linear in each of them. This is not the situation met by diatomic molecules, however, as the lowest-order model Hamiltonian displaying rotation-vibrational coupling is of third order in the quantum numbers.

We investigate in this paper the conditions for the appearance of cross-revivals of diatomic molecular wave packets. We start by finding general analytical relationships for it in the case of the lowest-order model molecular Hamiltonian. Next, we examine by numerical calculations the effect of including higher-order terms in the Hamiltonian using typical molecular parameters and finally we show that cross-revivals will take place generally with large amplitude, under certain circumstances, even for hot molecules.

II. THEORY AND CALCULATIONS

Let us start by expressing the time-dependent wave function of a rovibrational diatomic molecular wave packet in terms of the stationary eigenstates with vibrational quantum number v and rotational quantum number J,

$$\Psi(r,t)=\sum_{vJ} c_{vJ}\psi_{vJ}(r)\exp\{-iE_{vJ}t/\hbar\}, \tag{1}$$

and ignore possible perturbations, so that the term energies E_{vJ} can be represented by a Dunham expansion

$$E_{vJ}=\sum_{ij} Y_{ij}\left(v+\frac{1}{2}\right)^{i} J^{j}(J+1)^{j}. \tag{2}$$

Then, assuming that the wave packet is centered about some quantum numbers $\overline{v}$ and $\overline{J}$ and defining the new variables

$$n=v-\overline{v},$$

$$k = J - \bar{J}, \tag{3}$$

we can rewrite the wave function as

$$\Psi(r,t) = \sum_{nk} c_{nk}\psi_{nk}(r)\exp\{-i(E_{\bar{v}\bar{J}} + E_{nk})t/\hbar\}. \tag{4}$$

If we now limit the Dunham expansion (2) to the lowest order which encompasses vibrational and rotational revivals and also exhibits coupling of the vibrational and rotational motions, i.e., we keep the five terms Y_{00}, Y_{10}, Y_{20}, Y_{01}, and Y_{11}, we get

$$\Psi(r,t) = \sum_{nk} c_{nk}\psi_{nk}(r)\exp\left\{-\frac{i}{\hbar}\left(n\frac{t}{T_n^{cl}} + k\frac{t}{T_k^{cl}} + n^2\frac{t}{T_{nn}^{\rm rev}} + k^2\frac{t}{T_{kk}^{\rm rev}} + nk\frac{t}{T_{nk}^{\rm rev}} + nk^2\frac{t}{T_{nkk}^{\rm rev}}\right)\right\}, \tag{5}$$

where the for us uninteresting energy of the wave packet center has been subtracted. The T_x^y notation is adopted from Bluhm, Kostelecký, and Tudose [7] and is slightly extended, and

$$1/cT_n^{cl} = Y_{10} + 2Y_{20}\left(\bar{v} + \frac{1}{2}\right) + Y_{11}\bar{J}(\bar{J}+1),$$

$$1/cT_k^{cl} = Y_{01}(2\bar{J}+1) + Y_{11}\left(\bar{v} + \frac{1}{2}\right)(2\bar{J}+1),$$

$$1/cT_{nn}^{\rm rev} = Y_{20},$$

$$1/cT_{kk}^{\rm rev} = Y_{01} + Y_{11}\left(\bar{v} + \frac{1}{2}\right),$$

$$1/cT_{nk}^{\rm rev} = Y_{11}(2\bar{J}+1),$$

$$1/cT_{nkk}^{\rm rev} = Y_{11}. \tag{6}$$

We have for convenience introduced the speed of light, c (cm/s), as the unit conversion factor in Eq. (6), as conventional practice is to give the Dunham coefficients in terms of reciprocal centimeters.

Now, to gain clarity through reduced complexity but without sacrificing generality, the analysis can straightforwardly be extended to encompass the full problem, we limit the analysis to pump-probe experiments utilizing magic-angle configuration of linearly polarized laser fields [9]. The signal is then given by [1]

$$I_{\rm vib}(t) = \sum_J N(J)\sum_{i,j<i} A_{ij}[f^-(J) \times\cos\{2\pi ct(E_{v_iJ-1} - E_{v_jJ-1}) + \Delta\varphi_{ij}^{J-1}\} + f^+(J) \times\cos\{2\pi ct(E_{v_iJ+1} - E_{v_jJ+1}) + \Delta\varphi_{ij}^{J+1}\}], \tag{7}$$

in which $N(J)$ is the rotational population distribution in the initial electronic state and the $f^{\pm}(J)$ factors correspond to the statistical and orientational weights of the rotational transitions. The A_{ij}'s contain all other information on initial state population, transition probabilities, laser field frequency and intensity, detection probabilities, and so forth. The phase shifts describing the shape and position of the wave packet are denoted $\Delta\varphi_{ij}^{J\pm1}$.

The magic-angle signal contains only beat terms between energy levels with different v's and identical J's. Consequently, all terms in Eq. (4) which depend solely on k do not contribute to our signal. In other words all terms of the kind Y_{0j} of the Dunham expansion (2) are absent in the observed signal and are here henceforth ignored.

We apply the classical phase r-centroid approximation for the numerical computation of the signal (7). This model is detailed in Ref. [10] and we give here but a brief overview of its features and merits. The quintessence of the model is the semiclassical approximation to replace the phase shifts in Eq. (7) by the classical phase of the corresponding r centroids. This renders the calculations very inexpensive, even when including every relevant rovibrational transition at high temperature. Furthermore, the temporal dimension of the laser-molecule interaction is neglected, which is of little consequence here, as we are interested only in very long time scales so that the laser pulses are well separated in time. It must be noted, however, that the phase shifts in Eq. (7) are influenced by the temporal structure of the laser pulses. The model was in Ref. [10] shown to reproduce all observed quantum dynamical features of the studied model case, NaK molecules in the $A\,^1\Sigma^+$ state, the short time dynamics even quantitatively. All needed molecular parameters in the calculations are computed from known potential energy curves and Dunham parameters using the LEVEL 6.1 software [11].

For the sake of consistency, we apply the classical phase r-centroid model also to the calculations with the model Hamiltonian defined in Eq. (5). We then choose the phase factors determining the classical positions of the pump and probe transitions to be zero and the wave packet to have a shape parametrized by a Gaussian distribution in both vibrational and rotational quantum numbers. If we furthermore ignore the Hönl-London and orientation factors, this procedure amounts to calculating the square modulus of the autocorrelation function of a Gaussian wave packet, a method which was used by Vetchinkin and co-workers [12,13] to investigate pure vibrational revival structures of wave packets in Morse potentials.

III. RESULTS AND DISCUSSION

To disclose the effect of rotation-vibration coupling on the long-time wave-packet dynamics in diatomic molecules, we start by discussing the dynamics in the case of a minimal coupled model Hamiltonian and then proceed to investigate the effect of including successive terms of a molecular Dunham expansion. Finally, we do calculations on molecules, i.e., we apply the full Dunham expansion of the molecular Hamiltonian, under various realistic experimental conditions.

A. Minimal coupling Hamiltonian

Following the assumption of magic-angle configuration, the only parameters we need to consider in Eq. (5) are T_n^{cl},

TABLE I. Dunham coefficients, Y_{ij}, for the minimal coupling Hamiltonian chosen so as to make Eq. (5) periodic for $\overline{v}=10$ and $\overline{J}=20$.

Y_{ij} (cm^{-1})	$j=0$	1
$i=0$	0.000	0.500
1	312.575	-0.005
2	-3.075	0.000

$T^{\rm rev}_{nn}$, $T^{\rm rev}_{nk}$, and $T^{\rm rev}_{nkk}$. Each of these parameters corresponds to a distinct beat period of the vibrational transient. Thus, the classical vibrational period is given by T^{cl}_{n} and the vibrational revival time by $T^{\rm rev}_{nn}$. The rovibrational coupling generates the cross-revival and super-cross-revival times, $T^{\rm rev}_{nk}$ and $T^{\rm rev}_{nkk}$. The requirement for the overall function to be periodic and thus a full wave-packet revival to exist is that all four parameters are commensurate [6,7]. This is for the minimal coupling Hamiltonian always true for the relation between $T^{\rm rev}_{nk}$ and $T^{\rm rev}_{nkk}$ but generally not for the other relations. However, the various parameters give rise to near-periodic behavior whenever the beat periods are very different, as the beat periods then govern the envelope of the transient in a hierarchic manner. This is the normal case for the lowest-order anharmonic terms contributing to the magic-angle signal for diatomic molecules, that is, $T^{cl}_{n} \ll T^{\rm rev}_{nn} \ll T^{\rm rev}_{nk}$, as long as $\overline{J}$ is reasonably small. We defer momentarily the discussion of Hamiltonians with realistic molecular parameters, to study first the model case of a completely periodic minimal coupling molecular Hamiltonian (Table I) with parameters of molecular magnitude.

Extracting the cross terms from the exponent in Eq. (5) and using Eq. (6) we have

$$nk/T^{\rm rev}_{nk}+nk^2/T^{rev}_{nkk}=nkcY_{11}(2\overline{J}+1+k). \tag{8}$$

Thus, in the limit of $\overline{J}\gg k$ the molecular minimal coupling Hamiltonian becomes identical to the second-order Hamiltonian studied by Bluhm, Kostelecký, and Tudose in Ref. [8]. They showed that for such systems full cross-revivals occur with a period $T^{\rm rev}_{nk}$ and that the revival pattern with its system of fractional cross-revivals depends very much on the ratios between the revival periods. A peculiarity of the molecular minimal coupling Hamiltonian, however, is that $T^{\rm rev}_{nk}$ depends on $\overline{J}$. Thus, the cross-revival period will depend critically on the preparation of the molecular wave packet as well as on the potential.

Whenever the large-$\overline{J}$ limit does not hold, which is practically always, another characteristic of the molecular minimal coupling Hamiltonian becomes evident. To see this we consider the opposite limiting case, $\overline{J}\ll k$. Then Eq. (8) is dominated by the nk^2 term and we still have wave-packet revivals to occur whenever the exponent in Eq. (5) is a multiple of 2π, but now with period $T^{\rm rev}_{nkk}$. This is the longest period of all in Eq. (5) and it thus determines the full wave-packet revival period also in the cross-over regime between the two limiting cases. Note that $T^{\rm rev}_{nkk}$ contrary to $T^{\rm rev}_{nk}$ is independent of $\overline{J}$ and hence only depends on the potential.

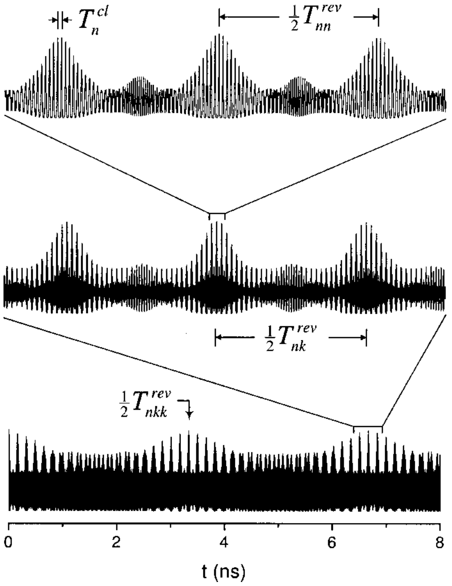

FIG. 1. Autocorrelation signal for a Gaussian wave packet with narrow J distribution ($\overline{v}=10$, $\Delta v=3$, $\overline{J}=20$, $\Delta J=2$) governed by the molecular minimal coupling Hamiltonian (Table I).

The two extreme limits discussed in the section above are idealized cases and are thus never met in experiments. Still, they turn out to be good approximations to the two realistic cases $\overline{J}>\Delta J$ and $\overline{J}\approx\Delta J$. The second case is typical of standard femtosecond pump-probe experiments on thermally excited molecules and the first one can be achieved either by cooling the molecules in a supersonic expansion or by using the labeling technique developed by Uberna *et al.* [14]. Applying the latter method, however, one has to remember that the standard conditions of magic-angle detection no longer apply, as they require an initially isotropic molecule ensemble.

Full wave-packet revivals occur in the $\overline{J}$ cross-over regime only at the super cross-revival period $T^{\rm rev}_{nkk}=1/cY_{11}$. Nevertheless, much of the $\overline{J}\gg\Delta J$ behavior is retained when $\overline{J}>\Delta J$ and the structure of first-order revivals is still prominent. This is exemplified in Fig. 1. Note that structures related to half-revivals with full magnitude but with the vibrational phase shifted by π are occurring on all time scales and that the beat pattern is symmetric around $\frac{1}{2}T^{\rm rev}_{nkk}$. At this time the even and odd wave functions are exactly out of phase with respect to each other. Other fractional revivals are seen in between the full revivals.

Broadening the population distribution over rotational states, so that $\overline{J}\approx\Delta J$, rapidly quenches the first-order cross-revivals and the fractional cross-revivals. Thus, we see in Fig. 2 sharp spikes of full super cross-revivals occurring at $T^{\rm rev}_{nkk}$ and little evidence of ordinary cross-revivals or revivals except for a couple of strong fractional cross-revivals.

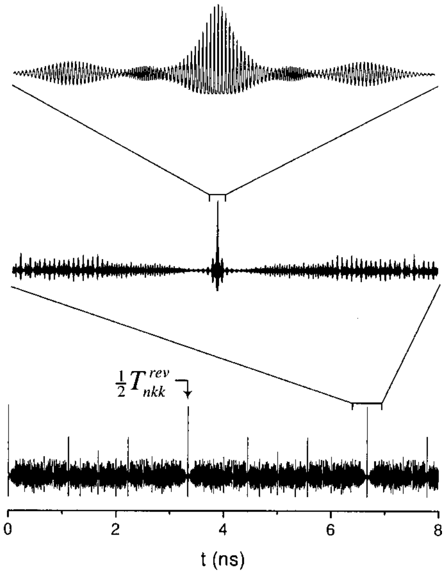

FIG. 2. Same as Fig. 1 except for the broader J distribution ($\overline{v}=10$, $\Delta v=3$, $\overline{J}=20$, $\Delta J=20$).

B. Higher-order Hamiltonians

Terms of higher orders will tend to wash out the cross-revival and super-cross-revival structures, to create new ones at even longer times. Their impact will, however, be very much dependent on the magnitude and signs of their respective scaling factors, in our case the Y_{ij}'s in the Dunham expansion (2). Especially due to the normally occurring alternation in sign and therefore partial cancellation of the various terms it is beforehand not obvious to what extent cross-revivals will take place for more complicated molecular Hamiltonians than the minimal coupled one discussed in Section III A.

To illuminate the behavior of higher-order Hamiltonians we calculate traces using Dunham expansions of various sizes. Some representative results for the $\overline{J}\approx\Delta J$ case, which is the case most prone to be affected by the dispersive effects of the higher-order cross terms, are reproduced in Fig. 3. The Dunham coefficients used in these calculations are those for Li_2 molecules in the $A\ ^1\Sigma_u^+$ state (Table II). Note, as the symmetry about $\frac{1}{2}T_{nkk}^{\mathrm{rev}}$ is now broken, we can, strictly speaking, not call the structure at $\frac{1}{2}T_{nkk}^{\mathrm{rev}}$ a half revival and we henceforth drop the distinction between half and full revivals.

Higher-order purely vibrational terms Y_{i0}, where $i>2$, will, due to the relatively small spread of the wave packets in v, for the first few super cross-revivals mainly affect the vibrational period and vibrational revival periods and amplitudes. A reduction of the super cross-revival amplitude is also clear but not severe, as $Y_{30}\ll Y_{11}$. Thus, we choose the minimal coupling Hamiltonian with all Y_{i0} terms to be our reference for discussing the effects of higher cross terms. The first super cross-revival of the reference Hamiltonian is shown in Fig. 3(a).

The dispersive action of the Y_{21} term is vividly born out in the cross-revival structure in Fig. 3(b). Not only is the structure broadened and therefore attenuated, it also moves to longer times by about 10%. However, the subsequent terms of the kind Y_{i1} in the Dunham expansion have the opposite sign to Y_{21} and largely cancel the detrimental effect of the latter, as is seen in Fig. 3(c). As a consequence, the cross-revival structure once again narrows, its magnitude increases, and the period shortens.

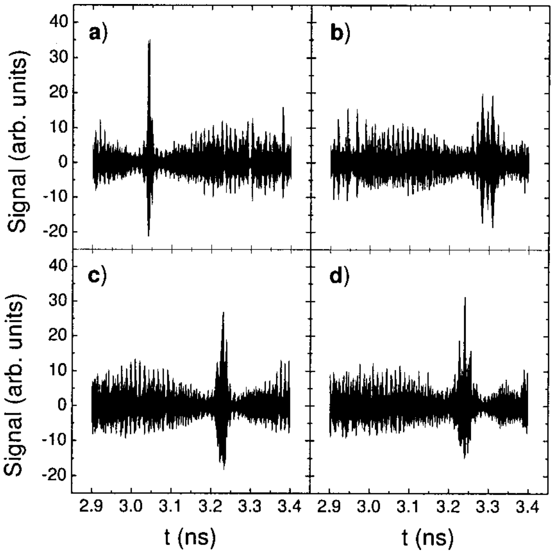

FIG. 3. The effect on the first super-cross-revival peak of the autocorrelation signal for a Gaussian wave packet ($\overline{v}=10$, $\Delta v=3$, $\overline{J}=15$, $\Delta J=20$) of including higher-order terms of the Hamiltonian. The Dunham expansion is that of the $\mathrm{Li}_2(A)$ state (Table II). The various terms included are (a) Y_{i0},Y_{01},Y_{11}; $i=0-5$; (b) Y_{21} added; (c) Y_{31},Y_{41} added; (d) all terms, respectively.

Adding even higher Y_{ij} terms, that is, with $j>1$, has relatively minor consequences for the overall appearance of the super cross-revival. Consequently, the super cross-revival for the full Hamiltonian in Fig. 3(d) is very similar to the preceding one and has even higher amplitude than it does. The final amplitude is actually about 80% of the original, which is a somewhat artificially high number. The ratio Y_{11}/Y_{20} for $\mathrm{Li}_2(A)$ is coincidentally very close to a half-integer value. As the initial super-cross-revival peaks are very narrow (see Fig. 2), the width is about the width of a vibrational revival peak, this means that the first (half) super cross-revival falls between two vibrational revivals and is strongly suppressed. This strong effect in turn is a consequence of the restriction of perfect phase alignment of the partial waves in the Gaussian wave packet, which is never present in a real experiment. Moreover, truly molecular wave packets will include more dispersive terms than Gaussian wave packets. All in all, similar simulations with realistic wave packets yield results comparable to those in Fig. 3, although with somewhat stronger effects. It thus seems as though only a small number of terms are important for the gross features of the super cross-revivals of Hamiltonians with parameters of molecular magnitude.

C. Molecular Hamiltonians

The concluding remark of the previous section indicates that cross-revivals might be observable in experiments on

TABLE II. Dunham coefficients, Y_{ij}, for the $\mathrm{Li}_2(A\ {}^1\Sigma_u^+)$ state [15].

Y_{ij} (cm^{-1})	$j=0$	1	2	3
$i=0$	0.000	$4.974\,237\,6\times10^{-1}$	$-7.468\,605\,3\times10^{-6}$	$9.750\,894\,3\times10^{-11}$
1	255.4673	$-5.480\,648\,6\times10^{-3}$	$6.542\,245\,2\times10^{-8}$	$-1.643\,478\,5\times10^{-12}$
2	$-1.581\,360\,6$	$2.005\,072\,7\times10^{-5}$	$-6.728\,066\,9\times10^{-10}$	0.000
3	$3.127\,908\,9\times10^{-3}$	$-1.558\,119\,9\times10^{-7}$	$-2.673\,592\,5\times10^{-11}$	0.000
4	$-3.463\,643\,2\times10^{-5}$	$-1.122\,497\,0\times10^{-8}$	0.000	0.000
5	$-1.188\,920\,2\times10^{-6}$	0.000	0.000	0.000

real molecules. The typical parameters accessible to the experimenter are then those of the pump and probe laser fields and the temperature of the molecule. Thus, we simulate visible UV ultrafast pump-probe experiments on molecules initially in the electronic ground state with some sort of thermal distribution over rovibrational states. It should be noted, though, that in many experiments it would be advantageous to use preparation laser fields in order to gain tighter control over the wave-packet properties. All effects of spontaneous emission and collisions are ignored in the simulations. This is in practice a serious limitation for most of the simulated molecular states, although not for $\mathrm{Li}_2(A)$, as discussed in Sec. III D.

We here report in detail the results of the simulations of various wave packets moving in the $\mathrm{Li}_2(A^1\Sigma_u^+)$ state. The pump-probe scheme we apply is $X\ {}^1\Sigma_g^+ \rightarrow A^1\Sigma_u^+ \rightarrow E\ {}^1\Sigma_g^+$, for which all states are well characterized [15,16], and the signal we assume to be proportional to the final total population of the E state. Although this is a specific case, we find from simulations involving other molecular states that the conclusions appear to be generally valid.

It is clear from the calculations on model wave packets in the two preceding sections that there exist two regimes of the cross-revival pattern depending on the wave-packet properties, notably the spread in rotational states. The two sets of wave-packet parameters correspond approximately to expansion-cooled and hot ($T > 300$ K) Li_2 molecules, respectively. Consider first the case of expansion-cooled Li_2 molecules, for which the simulation result is shown in Fig. 4. The outstanding feature of this figure is the strong super cross-revival pattern with an amplitude close to 90% of the initial beat amplitude. In between these nearly complete wave-packet revivals there is a close to symmetric structure of partial revivals, which is attributable to plain and fractional cross-revivals. All in all, these features are indicative of a narrow wave packet in J space, and $\Delta J \approx 5$ is indeed found to describe the wave packet well. Note, this is the effective width of the wave packet, which is affected by $\overline{J} \approx 3$.

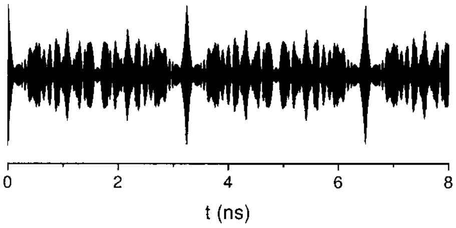

FIG. 4. Simulated pump-probe signal for cold $\mathrm{Li}_2(A)$. The initial population of the molecule is defined by $T_{\mathrm{vib}} = 70$ K and $T_{\mathrm{rot}} = 30$ K and the laser pulses have wavelengths $\lambda_{\mathrm{pump}} = 620$ nm and $\lambda_{\mathrm{probe}} = 800$ nm with a bandwidth of 200 cm^{-1} each.

The super cross-revival period in Fig. 4 is 3.245 ns. This is close to but longer than $\frac{1}{2}T_{nkk}^{\mathrm{rev}} = 1/2cY_{11} = 3.043$ ns, as expected in view of the results in Sec. III B. In that subsection a peculiarity of the $\mathrm{Li}_2(A)$ molecular constants Y_{11} and Y_{20} was pointed out, which lead to the first super cross-revival falling between two vibrational revivals. A magnified view of the first peak in Fig. 4 reveals just this characteristic. In conclusion, all features of Fig. 4 are qualitatively describable in terms of a minimal coupling Hamiltonian of the kind investigated in detail in Sec. III A. The higher-order terms are necessary for a quantitative description, though.

The parameters used in Fig. 3 correspond approximately to a wave packet produced at $T = 300$ K. Thus, we expect appreciable super cross-revivals to be present also at high temperatures. Setting the temperature to something typical of experiments in a heat-pipe oven, 900 K, yields the trace in Fig. 5. The super cross-revivals are as expected partially suppressed, but there is still a strong peak, 40% of the original amplitude, close to $\frac{1}{2}T_{nkk}^{\mathrm{rev}}$. It is found at a slightly longer time, however, 3.254 ns, than for the cold molecules. This is a reflection of the increased importance of the higher-order terms in the Hamiltonian, which tend to push the revival to later time (Sec. III B).

It might at first sight seem surprising that the cross-revival peaks survive the conceivably excessive thermal averaging of the signal at $T = 900$ K. The effective rotational temperature of the wave packet, however, is only 430 K, for two major reasons, both of which are related to the strict selection rules applying to the rotational quantum numbers in a two-photon transition. First, provided the laser wavelength bandwidth is sufficient, the J distribution in the excited state is very similar to that of the ground state. This means that the

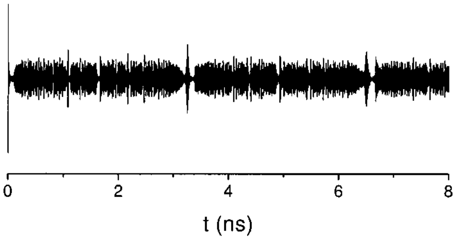

FIG. 5. Same as Fig. 4 except for $T_{\mathrm{vib}} = T_{\mathrm{rot}} = 900$ K.

effective rotational temperature in the excited state, T_{rot}^{*}, is different from that of the ground-state distribution, T_{rot}^{0}, as the rotational constants for the two states involved, B_{v}^{*} and B_{v}^{0}, are different. In the case of identical J distributions $T_{\mathrm{rot}}^{*}=(B_{v}^{*}/B_{v}^{0})T_{\mathrm{rot}}^{0}$, which in the excitation process yields a reduction of the effective rotational temperature, as typically B_{v}^{0} is greater than B_{v}^{*}. In the $\mathrm{Na}_2(A)\leftarrow\mathrm{Na}_2(X)$ transition, $B_{v}^{*}/B_{v}^{0}=0.67$, which is close to the observed cooling ratios 0.66, 0.63, and 0.63 at 300, 700, and 900 K, respectively. The same ratio of the rotational constants applies to the corresponding transition in Li_2, and a cooling ratio 0.68 is obtained for an initial temperature of 300 K. For the high-temperature case of 900 K, however, the cooling ratio is substantially lower, 0.48, which implies an additional cooling mechanism being effective.

The second process contributing to the ‘‘rotational cooling’’ of the wave packet is connected to the limited wavelength bandwidths of the laser pulses. Namely, if the differences between the three rotational constants in the pump-probe process [17] are sufficiently large, then the rotational distribution in the ground state is not fully sampled. The sampling efficiency is obviously related to the absolute size of the rotational constants, as smaller absolute values generally imply smaller differences. This in turn leads to that lighter molecules are more likely to experience the bandwidth related cooling than heavier ones. Consequently, as observed here, the laser bandwidths are sufficiently large to sample the Na_2 rotational distribution efficiently at all temperatures but not so for Li_2 at elevated temperatures. Thus, the wave packets generated in $\mathrm{Li}_2(A)$ at 900 K are cooled rotationally even more than expected from the simple rotational constant mechanism discussed above.

We have shown that super cross-revivals of vibrational wave packets in the unperturbed $\mathrm{Li}_2(A)$ state will occur with very large magnitude even at high initial molecular temperature. How general is this phenomenon? The ‘‘rotational cooling’’ due to changing rotational constants in the excitation process will be present for all transitions where the ground state is more strongly bound than the excited state, which is normally the situation, and thus it is a generally occurring process. The ‘‘cooling’’ due to bandwidth limitations is restricted to light molecules, however. Thus, the super cross-revivals for heavier molecules at high temperatures will not occur with as large amplitude as in Li_2. For $\mathrm{Na}_2(A)$ at an initial temperature of 900 K, e.g., we obtain a super cross-revival amplitude which is 17% of the initial vibrational amplitude. The same measure for initially cold ($T_{\mathrm{vib}}=50\,\mathrm{K}$, $T_{\mathrm{rot}}=10\,\mathrm{K}$) Na_2 molecules is 65%. Likewise expansion-cooled $\mathrm{NaK}(A)$ and $\mathrm{I}_2(B)$ molecules also yield strong super cross-revivals, 56% and 50% of the initial amplitude, close to $1/2T_{nkk}^{\mathrm{rev}}$. Although we have investigated merely a few molecular states, the high consistency of the results in the different cases indicates that the existence of cross-revivals and super cross-revivals is an inherent and therefore general feature of wave-packet dynamics in unperturbed diatomic molecular potentials and can be observed provided the initial molecular temperature is not too high. For molecules containing sufficiently light atoms the temperature restriction is relaxed, as the laser wavelength bandwidth then becomes a limiting factor.

D. Perturbation and lifetime effects

We ignored in the discussion above several commonly occurring complications to the simple picture of a wave packet moving under the influence of a potential. These effects have to be assessed in order to judge whether or not the super cross-revivals are a physical reality in molecules.

Considering that the cross-revival time scale ranges from a few ns for the lightest diatomic molecules to a couple of hundred ns for the heavier ones, it is clear that radiative lifetime effects will be detrimental to the cross-revivals of wave packets in most electronically excited states. In addition, collisions will scramble the phase of the wave packet whenever the ambient pressure is about a millibar or above, with the same end result.

The remedy for the collisional quenching is easily found by performing the experiments in molecular beams, which is anyway a prerequisite to obtain the low temperatures necessary to observe near-complete cross-revivals. The radiative lifetime on the contrary does not lend itself to such easy manipulation and restricts the number of molecular states for which cross-revivals are possible. As it turns out, cross-revivals of wave packets in electronically excited states with fully allowed optical transitions to lower states available, i.e., all states accessible by direct laser excitation from the electronic ground state, are only feasible for molecules containing at least one of the very lightest elements, such as lithium. In this context even sodium is a heavy atom. Our particular case of $\mathrm{Li}_2(A)$ is a good example of a case when T_{nkk}^{rev} is short enough compared to the fluorescence lifetime (19 ns [18]) to facilitate the existence of cross-revivals.

The obvious, although experimentally nontrivial, way to avoid the limitation of radiative lifetime is to do the experiments on molecules which are in a state not directly coupled to a lower one by a strong optical transition. This involves at least one preparation stage, for instance, in which a third laser field is applied. Such a scheme was, for example, recently [19] successfully employed to prepare and probe a wave packet in the electronic ground state of K_2. Another suitable approach, which simultaneously eliminates the need for expansion cooling of the molecules by applying a continuous-wave laser for highly selective initial state preparation, has been developed by Uberna *et al.* [14].

Finally, we have throughout the discussion assumed that the energy levels of the molecular states can be expressed by a simple Dunham expansion. It has to be kept in mind, though, that perturbations of electronically excited states by other nearby states may cause deviations from this behavior. The $A\ ^1\Sigma_u^+$ state of Li_2, for instance, is perturbed by the $a\ ^3\Pi_u$ state [18] and the perturbation will for some choices of wave-packet parameters alter the appearance of the cross-revival structures. This perturbation is caused by spin-orbit coupling and is very local. Hence, depending on the state composition of the wave packet, such perturbations may or may not have significant influence on the cross-revivals. In conclusion we note that perturbations are absent for the electronic ground state.

IV. CONCLUSION

We predict that vibration-rotation coupling in diatomic molecules will lead to cross-revivals of vibrational wave packets—provided lifetime effects and collisions can be eliminated. The cross-revivals we obtain are nearly complete for expansion-cooled Li_2 in the $A\,^1\Sigma_u^+$ state. Due to ‘‘rotational cooling’’ of the wave packet in the pump-probe process these cross-revivals survive thermal averaging and reach at 900 K an amplitude which is close to half the beat amplitude at zero time delay. Except for molecules containing at least one very light atom, one has to resort to experimental schemes involving preparation of wave packets in the electronic ground state to observe cross-revivals, as to avoid thermal averaging and/or lifetime effects to dominate the long time dynamics.

The detectable time correlation extending over many ns discussed here opens some interesting prospects. First, collisions in the gas phase at all reasonably normal temperature and pressure take place on a pico- to nanosecond time scale. Thus, information on various collisional cross sections might be extracted by monitoring the cross-revival structure as a function of pressure. Second, Uberna *et al.* [14] have shown the feasibility of utilizing phase control of molecular wave packets on a ps time scale and that it is in this fashion possible to ‘‘focus’’ the wave packet so that ionization occurs at a specified instance. From the results obtained here, it is clear that the same approach could in principle be applied to cross-revivals to obtain wave-packet focusing on a ns time scale. Finally, careful analysis of the cross-revival structure seems to be a potential tool to investigate perturbation phenomena in diatomic molecules.

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