High-Precision Molecular Wave-Packet Interferometry with HgAr Dimers

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Molecular wave-packet (WP) interferometry has been demonstrated in the A electronic state of the HgAr van der Waals complex with two time-delayed UV fs pulses at 254 nm. The interferograms of three vibrational levels in the WP's display almost 100% fringe contrast as a function of the interpulse delay τ, which is tuned with sub-10 as stability and resolution. It is clearly observed that the three interferograms show their dephasing and rephasing within a single vibrational period, allowing us to prepare arbitrary relative populations of the three levels by adjusting a single parameter τ.

Wave-packet (WP) autocorrelation [1] or WP interferometry (WPI) has been exemplified, using two identical time-separated optical pulses, for Rydberg WP's in atoms [2–15] and vibrational WP's in molecules [16–19]. The WPI, often referred to as Ramsey interferometry, can be viewed as (i) the interaction of two WP's or (ii) the interference of the optical pulses filtered by the atomic or molecular transitions [4,8,11]. The WPI is based on the measurement of population sensitive to the relative phase of the optical pulses. The individual measurement of the population of each eigenstate in a WP is desirable for developing coherent control of the state-to-state chemistry [20–27] and quantum logic gates based on the Ramsey interferometry [28]. While such state-selective WPI has been performed for the Rydberg atoms [2,6,7], it has scarcely been done in molecular systems, where, even if the vibrational states are resolved, the molecular rotation adds another complexity. The thermal distribution of rotational states is known to be a major source of decoherence in molecular systems that can wipe out the interference structure much more quickly than in atomic systems [16–18]. To minimize such effects a single precursor state could be selected out of the thermal distribution prior to WP generation [29–31]. We will demonstrate in this paper an alternate approach to vibrational and rotational state resolved WP interferometry to create a high-resolution molecular WP interferometer, where the rotational dephasing is drastically reduced by more than an order of magnitude, and arbitrary superpositions of vibrational eigenstates in the WP are selectively prepared.

Figure 1 illustrates our pump-control-probe scheme, and the experimental apparatus is essentially the same as that used in our previous fs laser study of the Hg-CO van der Waals (vdW) complex [32]. Briefly, the Hg-Ar vdW complex was prepared in the $\nu = 0$ level of the ground state ($X^1 0^+$) by the supersonic jet expansion of Hg/Ar mixture into a vacuum chamber through a pulsed

valve. The rotational temperature of the complex was 4 K [33], which is substantially lower than was used in the previous studies of molecular WP interferometry [16–18]. The output of a Ti:sapphire laser system was frequency tripled to generate a 300 fs UV pulse around 254.2 nm ($\sim$ 10 μJ, 10 Hz). This UV pulse was input to the "attosecond phase modulator (APM)," which is a Michaelson-type interferometer constructed in a vacuum chamber, to generate a phased pair of laser pulses. The interpulse delay τ was coarsely tuned by sliding a mechanical delay stage
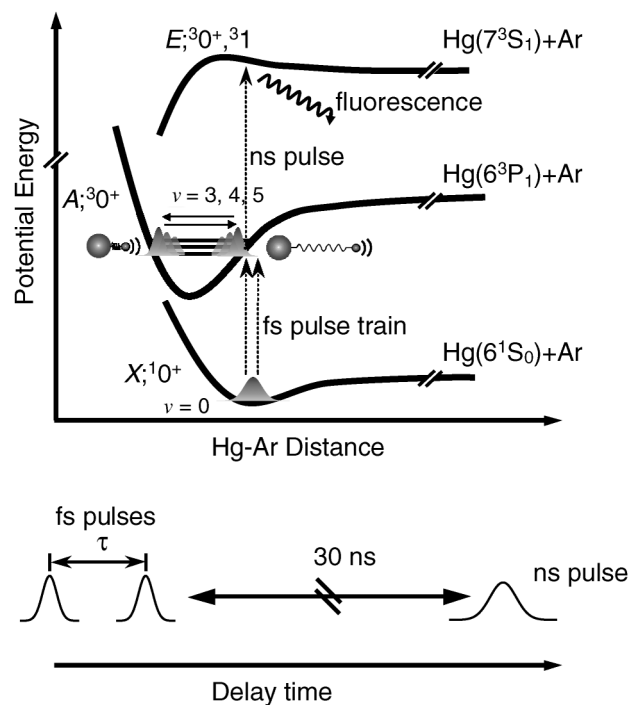

FIG. 1. Pump-control-probe scheme for detection of the populations of the A, ν' vibronic states created by a double-laser pulse from the $X, \nu'' = 0$ vibronic state.

placed in one of the arms of the APM, with a minimum step of about 1.7 fs. To obtain attosecond resolution in setting τ, we used pressure tuning of Ar or H_2 gas in a cell placed in the other arm. Our stability and resolution of τ is estimated to be 7 as [35]. The phased pair of fs pulses ejected from APM was directed collinearly to intersect the jet. An ensemble of about 10^{10} complexes was excited with an efficiency of about 2% by each of the fs pulses. The center wavelength of the pulses (254.2 nm) was selected so that the $\nu' = 3$, 4, and 5 vibrational eigenstates of the $A^3 0^+$ state were coherently superposed, and two molecular WP's were created sequentially near the outer turning point of the potential curve. A ns probe laser pulse was delayed by 30 ns from the fs pulses and was used for laser induced fluorescence (LIF) detection of the A state population. The bandwidth of the ns probe

laser was 0.05 cm^{-1}, and its wavelength was tuned to cover a small number of rotational lines with $J'' = 4$–8 within either the 15-3, 16-4, or 17-5 vibrational bands of the E-A transition. Combination of the narrow bandwidth of the probe laser and the low rotational temperature has enabled us to select a limited number of rotational states for a particular vibrational level of the A state.

Interpretation of the present experiment in terms of a standard linear-response theory is straightforward. The spectrum of the double pulse, $S(\omega, \tau)$, is

$$S(\omega, \tau) = 4s(\omega)\cos^2(\omega\tau/2), \qquad (1)$$

where $s(\omega)$ is the spectrum of one of the twin pulses. The population $n_{A,\nu',j'}$ of the rovibronic state A, ν', j' is

$$n_{A,\nu',j'} = \langle C_{X,\nu'',j'';A,\nu',j'} s(\omega_{X,\nu'',j'';A,\nu',j'})\cos^2(\omega_{X,\nu'',j'';A,\nu',j'}\tau/2)\rangle, \qquad (2)$$

where $\langle \cdots \rangle$ defines an average over the thermal distribution of vibrational and rotational states of the X state, and the coefficients C are related to the squared matrix elements of the transition dipole moment. As mentioned above, only the ground vibrational state $\nu'' = 0$ contributes, and averaging over the initial rotational distribution involves only two rotational states ($j'' = j' \pm 1$) due to the dipole selection rule. The present twin pulse spectrum is much broader than the width of the rotational bands, so that the rovibronic transition frequency $\omega_{X,\nu'',j'';A,\nu',j'}$ in s can be replaced by the rotationless vibronic transition frequency $\omega_{X,0,0;A,\nu',0} \equiv \omega_{0,\nu'}$. The averaging over j'' introduces a dependence of the state populations on the temperature of the initial ensemble.

The response $R(\omega_P, \Delta\omega_P, T)$ of the system to interrogation by the ns probe pulse with central frequency ω_P and spectral width $\Delta\omega_P$ is proportional to the total population of the states that fit into this window. Examples of the response spectrum are shown in Fig. 2.

In our case, the spectral width of the ns probe pulse is much smaller than the total rotational progressions, so that $R(\omega_P, \Delta\omega_P, T)$ can be represented as a partial summation of nonoverlapping rotational lines:

$$\begin{aligned} R(\omega_P, \Delta\omega_P, T) &\approx R_{\nu'}(\omega_{P,\nu'}, \Delta\omega_P, T) \\ &\approx \sum_{j' \in \omega_{P,\nu'},\Delta\omega_P} n_{A,\nu',j'}(T), \end{aligned} \qquad (3)$$

where the frequency $\omega_{P,\nu'}$ lies somewhere within a rotational band originating from the vibrational state ν'. Arbitrary normalized quantities $r_{\nu'} \propto R_{\nu'}^{\max}$ served as data points to construct the WP interferograms of three vibrational states, $r_{\nu'} = r_{\nu'}(\tau)$. Sample interferograms are shown in Figs. 3(a)–3(d) for small ranges (fs scale) of the delay time $\Delta\tau = \tau - \tau_0$ centered around a coarse setting τ_0 (ps scale). In going from Figs. 3(a)–3(d), τ_0 is displaced by a step of a quarter of the average vibrational period (about 0.25 ps), as seen from the lower panels

showing the relative positions of the two WP's when the second WP is created. The oscillation cycle of the interferograms is about 0.85 fs, which is very close to the inverse of the center frequency of the fs pulse. As indicated in Eq. (3), the expected harmonic dependence is affected by the averaging and the spectral width of the ns probe pulse since the molecules rotate during the interpulse delay τ. We call this effect delay-time rotational dephasing (DTRD). Clearly, DTRD distorts the expected harmonic behavior of $r_{\nu'}(\tau)$ more and more as τ increases. The observed behavior is also affected by instability in τ and by any deviation from perfect spatial overlap of the two fs pulses. All these factors induce a decrease in the fringe contrast. In the limit of the highest contrast, we can write

$$r_{\nu'}(\tau) \propto \cos^2(\omega_{0\nu'}\tau/2). \qquad (4)$$

Our interferograms in Fig. 3 reach almost to this limit, so that, for a given ν', each interferogram clearly measures the interference due to the phase shift between the two traveling fs pulses that are separated by more than 0.3 mm. The cyclic dephasing and rephasing of the three interferograms in Fig. 3 arises from different vibronic frequencies for the X; $0 \to A$; 3, 4, and 5 transitions. This is different from the well-known collapse and revival of a WP [36] that comes from small differences or anharmonicities in level spacings. While the idea of creating different interferograms associated with consecutive eigenstates in a WP has been mentioned previously for spin orbit [14], Rydberg [2,3,6], and vibrational [17] WP's, the present individual measurement of the interference pattern of each eigenstate has allowed us to directly observe such dephasing and rephasing of the interferograms.

Each point of the interferogram registers the result of the pump-control-probe sequence shown in Fig. 1. The duration of this sequence (30 ns) is essentially infinite
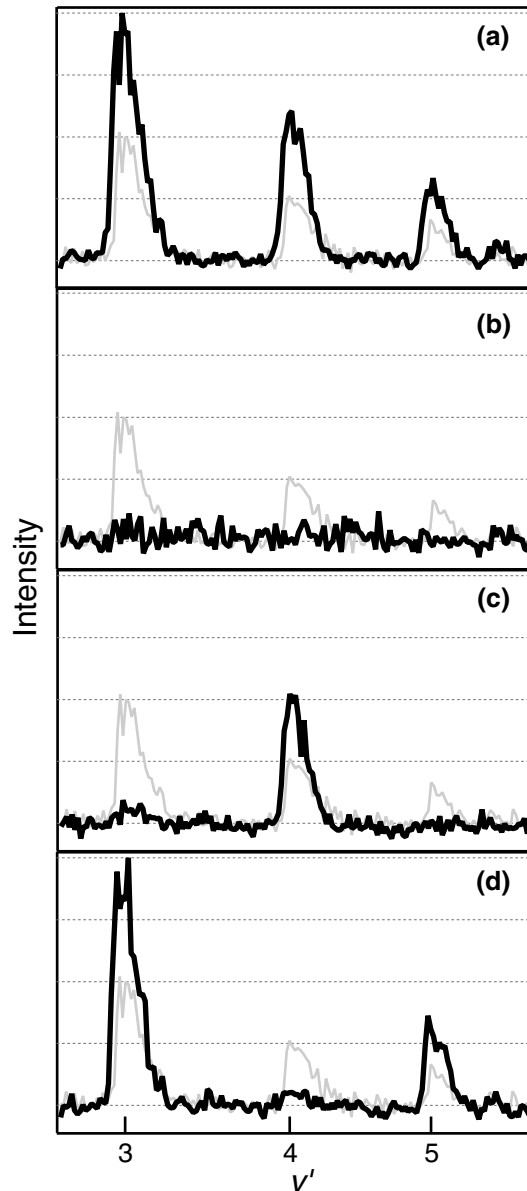
FIG. 2.   Examples of the response spectrum for double-pulse excitation as a function of the interrogating laser frequency for four different values of the interpulse-delay time τ; (a),(b) $\tau \sim 1T_{\mathrm{vib}}$; (c),(d) $\tau \sim 1.5T_{\mathrm{vib}}$, where $T_{\mathrm{vib}}(= 1.1 \text{ ps})$ is a classical vibrational period of the relevant vibrational eigenstates $\nu' = 3, 4, 5$. As reference, a response to a single pulse excitation is shown in the shaded spectrum with its vertical scaling expanded by a factor of about 2. For clarity, the laser frequency is translated into a dimensionless quantity running through the vibrational energy axis of the A state. Points $\nu' = 3, 4, 5$ correspond to the E-A transitions from rotationless vibrational states.

compared to the time scale of the molecular vibrations (1 ps), the temporal width of the twin pulses (300 fs), and the period of the optical cycle (0.85 fs) that produces the excitation. The diagonal elements of the density matrix, the state populations, do not depend on time after the
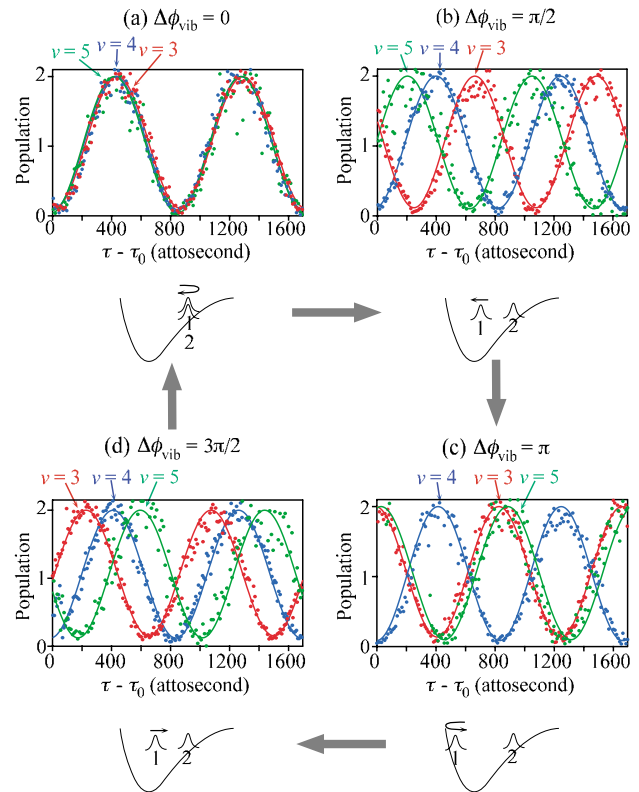

FIG. 3 (color).   Interferograms for the populations of vibronic states A, $\nu' = 3$, A, $\nu' = 4$, A, $\nu' = 5$ as a function of the delay time τ [the upper parts of (a)–(d)], and their WP interpretations [the lower parts of (a)–(d)] at the moment of creation of the second WP; (a) $\tau \sim 1T_{\mathrm{vib}}$; (b) $\tau \sim 1.25T_{\mathrm{vib}}$; (c) $\tau \sim 1.5T_{\mathrm{vib}}$; and (d) $\tau \sim 1.75T_{\mathrm{vib}}$, where $T_{\mathrm{vib}}(= 1.1 \text{ ps})$ is a classical vibrational period of the relevant vibrational eigenstates. WP1 is created at $t = 0$ in the region of the right turning point of the molecular potential of the A electronic state and then begins to oscillate as a classical particle. WP2 is created at time $t = \tau$ in the region of the right turning point, interferes with WP1, and the resultant WP evolves with a complicated interference structure. The quantity τ_0 denotes the value of the interpulse delay τ at the left edge of each graph.

pulse is over, and therefore they are determined by the property of the system just after the second pulse is finished. By the time of interrogation by the probe laser, all the interference structure of the WP density will be wiped out by rotational dephasing, and the WP density will be represented by a superposition of densities of three vibrational states with the weights determined by the delay τ and by DTRD. However these populations retain memory of the result of phase-sensing superposition of two WP's. One can create, therefore, virtually arbitrary relative populations of the three vibrational states by carefully adjusting τ.

Similar phase sensing and long-retained memory in atoms and molecules have been previously demonstrated for K [2] and Cs [6,7] atoms and Li_2 molecules [29–31]. For the atoms, different from molecular species, the

system is free from rotational dephasing. Similarly for Li_2, a single rotational level is selected as a precursor of a WP with a single mode cw laser so that the rotational dephasing is negligible. In the present study, in turn, all of the thermally distributed rotational levels are involved in WP's, so that decoherence should be much faster than the previous three cases. Still we have demonstrated that information can be vividly memorized in the ensemble of molecules and read out even after the coherence is wiped out, as seen in Fig. 2. This is due to our very slow DTRD (less than 4% loss in the fringe contrast within a single molecular vibration) insured by our cold (about 4 K) and dilute ensemble generated by the supersonic jet expansion and is due to narrow-band (0.05 cm^{-1}) interrogation of the state populations by the LIF technique.

In summary, we have observed, for a dilute ensemble of the HgAr vdW complex, a high-resolution interference of each individual vibrational level in WP's created by two time-delayed UV fs pulses at 254 nm. The interferograms of consecutive vibrational levels show their dephasing and rephasing within a single vibrational period, and display almost 100% fringe contrast as a function of the interpulse delay τ tuned with sub-10 as stability and resolution. Moreover, using this high precision interferometer, we have succeeded in creating virtually arbitrary relative superpositions of the three vibrational eigenstates within a WP only by tuning a single parameter τ. Finally, we point out that the interference structure can be reconstructed from the population information stored in the thermal ensemble of molecules during its radiative lifetime even after the coherence is wiped out. All these features are quite general in WP interference and therefore provide a basis for opening a new perspective of coherent control in a wide variety of quantum systems.

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