

A THEORETICAL STUDY OF THE DYNAMICS OF VIBRATIONAL WAVE PACKETS IN THE 1_g STATE OF Xe_2

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We present a theoretical description of the dynamics of vibrational wave packets in the 1_g state of Xe_2 . As an illustration, a simulation of a picosecond pump excitation–probe ionization laser experiment is carried out. The initial wavepacket is calculated using an explicit modelling of the short-pulse excitation process and propagated for up to 160 picoseconds. Evidence of fractional and full revivals of the wavepacket has been found and analyzed. The time delayed ionization signal is simulated using first order perturbation theory and shows clear oscillations corresponding to the temporal development of the wavepacket.

Keywords: Wavepackets; pump-probe spectroscopy

1. INTRODUCTION

In recent years there has been considerable interest in time-resolved experiments by means of ultrashort laser pulses (for a review, see Ref. [1]). For molecular systems, with bound potential energy surfaces, a pump laser pulse creates a coherent superposition of rovibrational states known as a wavepacket. This wavepacket initially oscillates between the classical inner and outer turning points of the potential with a periodicity determined by the local energy spacing between vibrational states. Because of the anharmonicity of the potential the

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wavepacket spreads quickly. However, at specific times interesting partial localization of the wavepacket can take place causing what are known as fractional revivals. Experimentally the evolution of the wavepacket can be monitored using a time-delayed probe laser pulse which ionizes the molecule. The ionization signal will show oscillations that reflect the fact that the vibrational overlap between the wavepacket and vibrational levels of the molecular ion depends on time. If the internuclear equilibrium distance of the excited state is larger than that of the ionic state the probability of ionization will be greater when the wavepacket is near to inner turning point of the potential. To date, vibrational wave packets have been experimentally observed for I_2 [2–3], Na_2 [4], Cs_2 [5], NaI [6], NaK [7], Li_2 [8], Br_2 [9], which have typical vibrational periods of several femtoseconds requiring laser pulses with similar durations. The Xe_2 molecule presents the main advantages: (1) The vibrational period is of the order of picoseconds, (2) the difference in equilibrium distances for $Xe_2(1_g)$ and $Xe_2^+(A^2\Sigma_u)$ states is $\Delta R \approx 4.2 a_0$ which implies a very narrow Franck–Condon detection window, therefore the ionization signal must oscillate as function of the time delay, (3) Xe_2 is an interesting system for observing high order fractional revivals only so far observed for Br_2 [9].

2. THEORY

The electronic potentials of Xe_2 are represented by Morse functions with molecular constants fitted to the available spectroscopic data [10–12]. We assume that the molecule is in its ground electronic and vibrational state, *e.g.*, following supersonic expansion. The theoretical description of the pump pulse excitation and subsequent propagation of the wavepacket is accomplished using the FFT split operator method [13–14]. The nuclear wave functions for the ground state $\psi_g(\{R_m\}, t)$ and the excited state $\psi_u(\{R_m\}, t)$ are evaluated at the spatial grid points $\{R_m\}$. The wavefunctions at $t + \delta t$ are calculated using the short time propagator:

$$\begin{pmatrix} \psi_g(\{R_m\}, t + \delta t) \\ \psi_u(\{R_m\}, t + \delta t) \end{pmatrix} = e^{-i((\hat{H}/\hbar)\delta t)} \begin{pmatrix} \psi_g(\{R_m\}, t) \\ \psi_u(\{R_m\}, t) \end{pmatrix} \quad (1)$$

where the time evolution operator is split into two parts corresponding to the kinetic and potential energy operators:

$$e^{-i(\hat{H}/\hbar)\delta t} \approx e^{-i(\hat{P}^2/2\mu)(\delta t/2\hbar)} e^{-i\hat{V}(\{R_m\},\delta t)/\hbar} e^{-i(\hat{P}^2/2\mu)(\delta t/2\hbar)} \quad (2)$$

$\hat{V}(R, t)$ is the potential matrix that contains the electronic diagonal potentials and the non-diagonal radiative coupling:

$$\hat{V}(R, t) = \begin{pmatrix} V_g(R) & V_{ug}(R, t) \\ V_{ug}(R, t) & V_u(R) \end{pmatrix} \quad (3)$$

We assume that the laser pulse has a Gaussian profile so the laser-molecule interaction is taken to be:

$$V_{ug}(R, t) = -E_0\mu_{ug}(R) e^{-t^2/\tau^2} \cos(\omega t) \quad (4)$$

where the temporal full width at half maximum is $\Delta t = 2\tau_p(\ln 2)^{1/2}$, ω is the mean carrier frequency, E_0 is the peak amplitude of the electric field and $\mu(R)$ is the transition dipole moment. The kinetic energy operator is defined in the momentum representation, and the potential operator in coordinate space, using the diagonal representation of the potential matrix $\hat{V}(R, t)$. The transformation of the wavefunction back and forth from coordinate to momentum space is performed using a Fast Fourier Transform (FFT) Danielson-Lanczos algorithm. The wavefunction on the ionic potential created by the probe pulse is a function of two different times: the time delay t_d between the pump and probe pulses and the total time. In the case of low laser intensities a perturbative methodology can be used without loss of accuracy. Following the theoretical approach described by Engel *et al.* [15] the nuclear wavefunction created by the probe pulse in first-order perturbation theory is:

$$\begin{aligned} \psi_I(R, t, \varepsilon_k) = & -\frac{1}{i\hbar} \int_{t_d}^t dt' e^{-i(\hat{H}_I/\hbar)[t-(t'-t_d)]} \mu_{Iu}(R, \varepsilon_k) \\ & \times E(t' - t_d) e^{-i(\hat{H}_u/\hbar)[t-(t'-t_d)]} \psi_u(R, t_d) \end{aligned} \quad (5)$$

where:

$$E(t' - t_d) = E_0 e^{-(t'-t_d)^2/\tau^2} e^{-i(\omega - \varepsilon_k/\hbar)(t'-t_d)} \quad (6)$$

where ε_k is the kinetic energy of the photoelectron. We assume that μ_{Iu} is constant over the interval $[0, \varepsilon]$ and zero otherwise. The corresponding probability of photoionization at time delay t_d between the two pulses is:

$$P_I(\varepsilon_k, t_d) = \lim_{t \rightarrow \infty} \int_0^\infty dR |\psi_I(R, t, \varepsilon_k)|^2 \quad (7)$$

and the total ionization probability:

$$P_I(t_d) = \int_0^\varepsilon d\varepsilon_k P_I(\varepsilon_k, t_d) \quad (8)$$

$P_I(t_d)$ is proportional to the ionization signal $S(t_d)$, that is, the yield of photoelectrons or molecular ions detected. In practice the integral over the electron kinetic energies is performed over an equidistant grid of discrete energies ε_k .

3. RESULTS AND DISCUSSION

In order to simulate the pump laser pulse we have chosen a central wavelength $\lambda = 293.3$ nm with a pulse FWHM of $\Delta t = 3$ ps ($\Delta\omega = 10$ cm⁻¹) and intensity $I = 10^{10}$ W/cm². At this wavelength the absorption of two photons is required to reach the 1_g state [12]. The probe pulse has identical parameters but with $\lambda = 363.4$ nm. The transition dipole moments μ_{ug} and μ_{ul} are not known so we have set them to be independent of the internuclear distance (Condon approximation). In order to evaluate the integral (7) an energy step $\delta\varepsilon_k = 2 \times 10^{-5}$ Hartree has been chosen and we have expanded the nuclear wavefunction created in the ionic state in the set of vibrational levels of the ground ionic state $\text{Xe}_2^+(A^2\Sigma_u)$.

Figure 1 shows some snapshots of the calculated wavepacket $|\phi(R, t)|^2$ to illustrate its evolution. A detailed analysis of revivals on Morse-like anharmonic systems has been given by Vetchinkin *et al.* [16]. They showed that the revival times hold the relation $t = p/q T_{\text{rev}}$ with p and q are integers. In this study we have observed revivals at times $t = 1/3 T_{\text{rev}}$, $t = 1/2 T_{\text{rev}}$, $t = 2/3 T_{\text{rev}}$ and $t = T_{\text{rev}}$.

The quantity that could be measured experimentally is the Xe₂⁺ or photoelectron signal as a function of the time delay between the pulses t_d . The ionization signal $S(t_d)$ is plotted in Figure 2a. The Franck–Condon factors between the levels $\nu = 11–18$ of 1_g and those of the

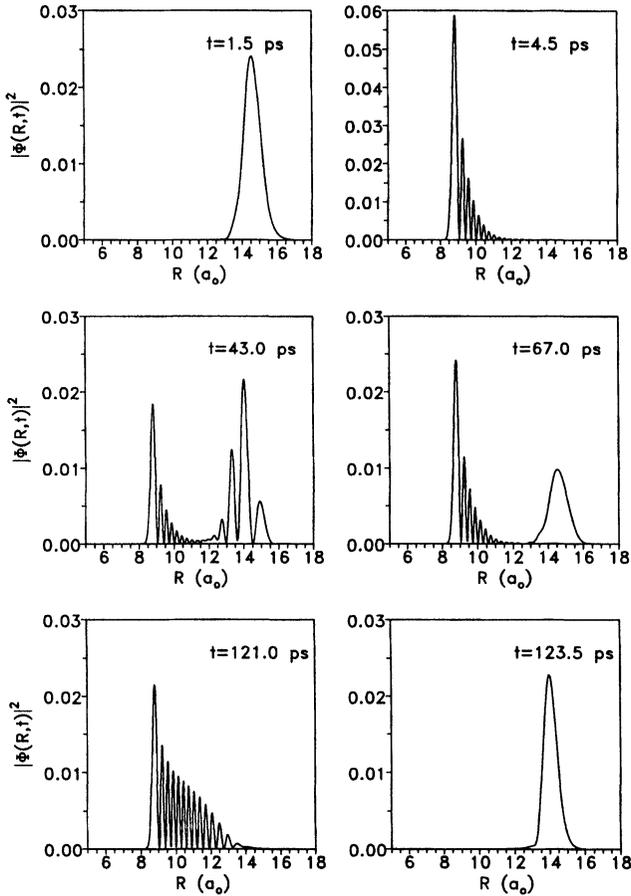


FIGURE 1 Snapshots of the wavepacket at several times in its evolution. The initial wavepacket at the end of the pump laser pulse is located at the outer turning point ($t = 1.5$ ps). The wavepacket shows interference patterns when the wave front reaches the inner turning point ($t = 4.5$ ps). Revivals of the wavepacket at longer times can be observed. At $t = 67.0$ a quarter revival takes place where the wavepacket has split into two sub-wavepackets. At $t = 123.5$ it has rephased completely, *i.e.*, full revival occurs, and is like the original one.

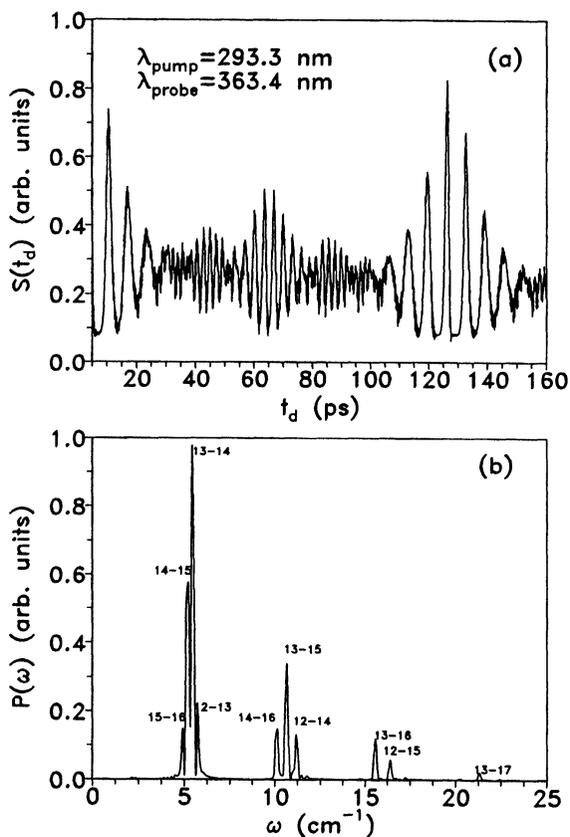


FIGURE 2 (a) Total ionization signal as a function of delay time; (b) Fourier transform power spectra of $P_I(t_d)$.

state $\text{Xe}_2^+(A^2\Sigma_u)$ dictated that only the levels $v^+ = 45-58$ are effectively populated. The Franck-Condon region is noticeably narrow so the photoionization only takes place when the wavepacket is close to the inner turning point of 1_g state. Further information about the frequencies contained in the ionization signal can be obtained by calculating its Fourier transform or Power spectrum $P(\omega)$, Figure 2b, the observed frequencies correspond to beats between the vibrational levels that compose the wavepacket.

4. CONCLUSIONS

We have carried out wavepacket calculations to model a picosecond pump-probe experiment on the Xe dimer. A fully quantum mechanical approach has been used to describe the pump pulse excitation, propagation of the wavepacket and the probe pulse ionization processes. In this study we have observed fractional revivals where the wavepacket splits into several sub-wavepackets, each oscillating at a classical frequency but shifted against each other. The predicted ionization signal shows clearly that this system is a prototypical example for vibrational wavepacket observations.

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References

- [1] Manz, J. and Wöste, L. Eds. (1995). *Femtosecond Chemistry*, Vols. 1 + 2 (VCH Verlagsgesellschaft mbH, Weinheim, Germany).
- [2] Fischer, I., Vrakking, M. J. J., Villeneuve, D. M. and Stolow, A. (1996). *Chem. Phys.*, **207**, 331.
- [3] Gruebele, M. and Zewail, A. H. (1993). *J. Chem. Phys.*, **98**, 883.
- [4] Baumert, T., Grosser, M., Thalweiser, R. and Gerber, G. (1991). *Phys. Rev. Lett.*, **67**, 3753.
- [5] Rodriguez, G., John, P. C. and Eden, J. G. (1995). *J. Chem. Phys.*, **103**, 10473.
- [6] Rose, T. S., Rosker, M. J. and Zewail, A. H. (1989). *J. Chem. Phys.*, **91**, 297.
- [7] Berg, L. E., Beutler, M. and Hansson, T. (1996). *Chem. Phys. Letters*, **253**, 327.
- [8] Papanikolas, J. M., Williams, R. M., Kleiber, P. D., Hart, J. L., Brink, C., Price, S. D. and Leone, S. R. (1995). *J. Chem. Phys.*, **103**, 7269.
- [9] Vrakking, M. J. J., Villeneuve, D. M. and Stolow, A. (1996). *Phys. Rev. A*, **54**, R37.
- [10] Freeman, D. E., Yoshino, K. and Tanaka, Y. (1974). *J. Chem. Phys.*, **61**, 4880.
- [11] Koechoven, S. M., Buma, W. J. and de Lange, C. A. (1995). *J. Chem. Phys.*, **102**, 4020.
- [12] Lu, Y., Morioka, Y., Matsui, T., Tanaka, T., Yoshii, H., Hall, R. I., Hayaishi, T. and Ito, K. (1995). *J. Chem. Phys.*, **102**, 1553.
- [13] Feit, M. D. and Fleck, J. A. (1983). *J. Chem. Phys.*, **78**, 301.
- [14] Heather, R. W. (1991). *Comput. Phys. Commun.*, **63**, 691.
- [15] Meier, Ch. and Engel, V. (1995). *Femtosecond Chemistry*, (Manz and Wöste, Weinheim), Chap. 11, pp. 369–394.
- [16] Vetchinkin, S. I. and Eryomin, V. V. (1994). *Chem. Phys. Letters*, **222**, 394.