

Wave Packet Structure and Dynamics Measured by Coulomb Explosion

H. Stapelfeldt,¹ E. Constant,^{1,2} and P. B. Corkum¹

¹Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6

²Departement de Physique, Faculté des Sciences, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1
(Received 22 December 1994)

The motion and dimension of molecular nuclear wave packets produced by an ultrashort laser pulse are measured by Coulomb explosion induced by a delayed intense fs laser pulse. Two different continuum wave packets in I_2 are observed as they move from an internuclear separation of ~ 7 to >100 Å. The ultimate spatial resolution is limited by the pulse duration of the probe laser. For 485 nm excitation of B -state wave packets the resolution limit is ~ 0.5 Å.

PACS numbers: 33.80.Rv, 34.50.Gb

Ultrafast phenomena in atoms and molecules studied by ps and fs laser pulses have been a topic of intense investigations over the past decade (see, e.g., the overviews of Refs. [1,2]). In atomic systems coherent superpositions of electronic wave functions forming angularly or radially localized wave packets are observed [2]. In molecules ultrashort laser pulses are used, for example, to study vibrational and rotational motion [1] and to investigate photofragmentation dynamics of clusters [3]. In a typical experiment a "pump" laser pulse excites a wave packet in the atom or molecule, and a second, delayed, "probe" laser pulse induces a transition to some final state. The observed signal exhibits a characteristic time-periodic structure if the transition caused by the probe only occurs efficiently at certain periodic values of the delay determined by, e.g., the Franck-Condon overlap between vibrational states [1] or by the electronic wave function's overlap with the atomic core [2]. To observe the wave packet anywhere on its trajectory Walmsley and co-workers [4] have suggested recording the spectral composition of spontaneous radiation emitted by molecular wave packets at each moment of time. A first experiment along these lines was reported recently [5]. Also, fs time-resolved photoelectron spectroscopy [6] has been proposed as a way to measure the structure and dynamics of wave packets, and experiments are now initiated [7].

Scattering femtosecond bursts of short wavelength (≤ 1 Å) particles such as photons [8] (≥ 12 keV), electrons [9] (≥ 150 eV), or ions (≥ 0.08 eV) from a molecule is a more direct approach to observing molecular wave packets. Since these particles must be prepared, synchronized, and transported through the interaction region with femtosecond precision, there are experimental difficulties, and no experiments have carried out where fs dynamics is measured by scattering.

The experimental problems simplify if we can use electrons or ions originating from the molecule itself employing a (delayed) fs laser pulse. In particular, for ion scattering, the half collision of an optically driven Coulomb explosion provides a simple, direct approach to measuring wave packets. Coulomb explosion of molecules following the collision between a thin

foil and a fast molecular-ion beam can be used to obtain information about molecular structure [10]. Here we demonstrate that a Coulomb explosion induced by irradiating molecular wave packets with an intense fs laser pulse is a straightforward and easy interpretable method to measure the motion and the dimension of wave packets.

The basic idea as applied to I_2 is illustrated in Fig. 1. First, a linearly polarized, ultrashort laser pulse excites a dissociative wave packet of continuum states. The wave packet is launched either in the $B^3\Pi_u^+$ or in the $1^1\Pi_u^+$ state. Second, the wave packet evolves along the respective potential curve. Third, the wave packet is exposed to an intense, delayed ultrashort pulse which causes rapid ejection of several electrons from the molecule. This corresponds to excitation of one (or several) repulsive states of the highly charged molecular ion. The residual atomic iodine ions repel each other due to the Coulomb force (Coulomb explosion). Since the removal of the electrons occurs on a time scale (≤ 100 fs) where the dissociated

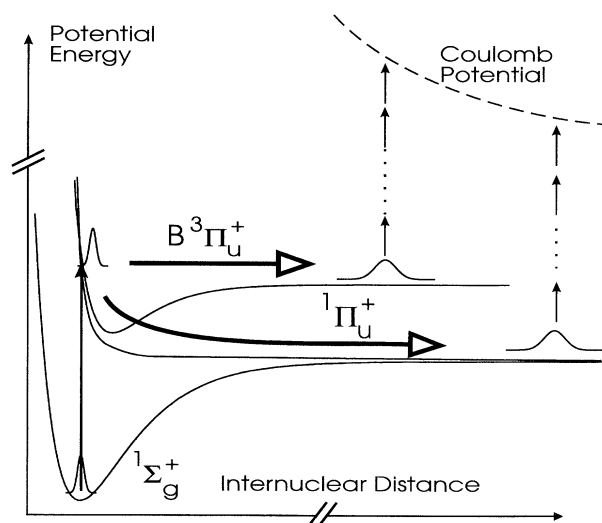


FIG. 1. Potential curve diagram of I_2 illustrating the preparation of the wave packet in either the $B^3\Pi_u^+$ or in the $1^1\Pi_u^+$ state and the subsequent probe process by excitation of a repulsive Coulomb state.

molecular constituents virtually do not move, the internuclear distance of the molecule can be determined by measuring the Coulomb energy, released as kinetic energy of the atomic ions. In addition, the spread of the observed kinetic energy reflects the width (dimension) of the wave packet. We stress that this scenario is accurate at sufficiently large internuclear separations (≥ 6 Å). At shorter distances the kinetic energy release is expected to deviate from the Coulomb value due to molecular bonding. Partly for this reason, our experiment concentrates on large internuclear separations, but the application of the Coulomb explosion to the short internuclear range is of great interest as we shall discuss later.

A diagram of the experimental setup is shown in Fig. 2. The output from a colliding pulse mode-locked (CPM) laser is amplified at 10 Hz in a four-stage dye amplifier [11] yielding a ~ 80 fs, 625 nm, ~ 250 μ J pulse. Part of the amplified pulse (~ 60 μ J) is used for continuum generation by focusing it into a 1.2-m-long cell filled with 25 atm of CO₂. A narrow bandpass filter selects 10 nm from the continuum centered at 485 nm. Amplification in a double-pass dye cell brings the 485 nm pulse energy up to ~ 200 nJ. The dye cell is longitudinally pumped by an UV (312 nm) pulse obtained from the second harmonic generation of another fraction (~ 130 μ J) of the amplified 625 nm pulse in a 5-cm-long KDP crystal. The 300 fs, 485 nm pulse is combined with the remaining ~ 60 μ J of the 625 nm pulse in a dichroic mirror, and both beams are focused inside the ultrahigh vacuum (UHV) chamber by an on-axis parabolic 5-cm focal-length mirror, giving a maximum intensity of $\sim 1 \times 10^{12}$ W/cm² and $\sim 9 \times 10^{14}$ W/cm², respectively. The zero time delay between the two pulses as well as the 485 nm pulse duration are determined by cross correlation.

Molecular iodine is leaked into the UHV chamber where the background pressure is 3×10^{-9} Torr. The I₂ pressure is kept low $\sim 5 \times 10^{-8}$ Torr in order to avoid any influence from space charge. The ions produced from the laser irradiation are analyzed in a time-of-flight (TOF) spectrometer [12]. It consists of an accelerating (electric field ~ 133 V/cm) and a field-free drift zone equipped with a dual microchannel-plate (MCP) detector at the end. The measured time of flight reflects the ion velocity along

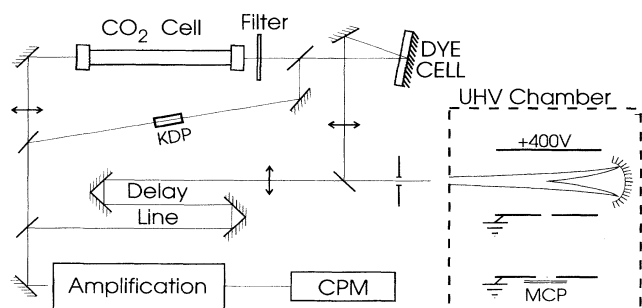


FIG. 2. A schematic of the experimental setup showing the fs laser system and the UHV chamber.

the spectrometer axis. Two apertures at the output of the accelerating and the field-free region ensure that we only observe fragments with their velocity vector essentially aligned with the TOF axis. Furthermore, the size of the apertures defines the acceptance angle of the spectrometer and to what extent the measured velocity corresponds to the real ion velocity. Finally, time-of-flight spectra are recorded using a digital oscilloscope with a sampling rate of 10^9 /s.

The experimental results are shown in Fig. 3. The curves show the I²⁺ TOF spectrum for different time delays between the blue and the red pulses. A symmetric structure consisting of two main peaks is observed corresponding to ionic fragments ejected either opposite to or in the direction of the detector. The distance between the symmetric peaks reflects the kinetic energy of the ions. The central feature of the spectra is that this distance decreases monotonically as the time delay increases (that is, as the excited wave packet evolves toward larger internuclear distances). The reduced amplitude of the wave packet signal at short time delays is caused by the decrease of the acceptance angle of the TOF spectrometer as the kinetic energy E_{kin} of the ionic fragments increases. This collection efficiency scales approximately as $1/E_{kin}$ in good agreement with the spectra of Fig. 3. It has been shown [13] that irradiation of I₂ at 485 nm leads to excitation of the $^1\Pi_u^+$ state if the polarization of the laser is perpendicular to the internuclear axis and excitation of the $B^3\Pi_u^+$ state if the polarization is parallel to the internuclear axis. Since the detection system selects molecules aligned with the TOF axis, the spectra in Fig. 3(a) (polarization of 485 nm beam perpendicular to the TOF axis) and Fig. 3(b) (polarization of 485 nm beam parallel to the TOF axis) correspond to a wave packet launched in the $^1\Pi_u^+$ state and in the $B^3\Pi_u^+$ state, respectively. Ions originating from Coulomb explosion of ground state molecules

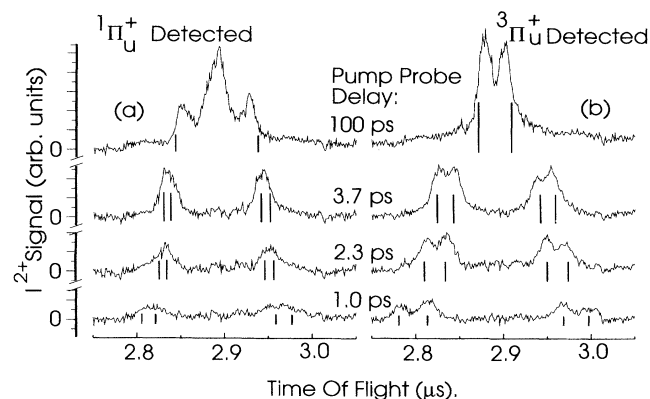


FIG. 3. The TOF spectrum of I²⁺ recorded at four different time delays between the blue and the red laser pulse. Each spectrum represents an average of 20 000 laser pulses. (a), (b) Observation of the $^1\Pi_u^+$ and the $B^3\Pi_u^+$ wave packet, respectively. The vertical lines represent the calculated positions of the different Coulomb explosion channels (see text).

are mainly ejected in the direction of the polarization of the red laser [12] which is perpendicular to the TOF axis. Even though the contribution to the ion signal from these unexcited molecules is small, all data are corrected by subtracting spectra recorded with the red laser only from the spectra recorded with both lasers. We note that the blue laser is not intense enough to ionize I_2 , so no signal is observed in the TOF spectrum if only the blue laser is applied.

The time difference ΔT between pairs of peaks is given by $\Delta T = 2m_1v_0/qeE$, where m_1 is the mass of atomic iodine (127 amu), E is the electric field strength in the accelerating region, qe is the charge of the observed ion, and v_0 is the initial velocity of the ion. This velocity is determined by the Coulomb energy and the wave packet motion:

$$\frac{1}{2} m_1 v_0^2 = \frac{1}{2} \frac{qq'e^2}{4\pi\epsilon_0 R} + \frac{1}{2} m_1 \left(\frac{v_{WP}}{2}\right)^2, \quad (1)$$

where R is the internuclear separation, $q'e$ is the charge of the other ejected ion, and v_{WP} is the dissociation velocity of the wave packet. Combining the expression for ΔT with Eq. (1) we get

$$\Delta T = \frac{1}{E} \sqrt{\frac{q' m_1}{q \pi \epsilon_0 R} + \frac{m_1^2 v_{WP}^2}{q^2}}. \quad (2)$$

The $B^3\Pi_u^+$ state and the $^1\Pi_u^+$ state dissociates at an energy of ~ 20044 and ~ 12441 cm^{-1} [14], respectively, and the average photon energy of the blue pulse is ~ 20621 cm^{-1} . Taking into account the distribution of vibrational levels in the ground state (see discussion later in the text) and the Franck-Condon overlap with the excited states we find a mean wave packet velocity of ~ 5.5 $\text{\AA}/\text{ps}$ in the $B^3\Pi_u^+$ state and ~ 17.8 $\text{\AA}/\text{ps}$ in the $^1\Pi_u^+$ state. Furthermore, from the shape of the potential curves we estimate the temporal evolution of the internuclear separation ($t \geq 0.3$ ps):

$$R(t/\text{ps}) = 5.5t + 3.9 \text{ \AA}, \quad B^3\Pi_u^+ \text{ state,}$$

$$R(t/\text{ps}) = 17.8t + 2.0 \text{ \AA}, \quad ^1\Pi_u^+ \text{ state.}$$

A conspicuous feature in Fig. 3 is the complex peak structure of the TOF spectra which results from explosions into different charge states. Using Eq. (2) and the expressions for $R(t)$ the expected positions for the two major fragmentation channels, $I^{2+}-I^+$ (2-1), $I^{2+}-I^{2+}$ (2-2), are indicated in Fig. 3 as vertical lines. The agreement with the TOF spectra is good. In particular, for small time delays it is seen how the substructure in the $B^3\Pi_u^+$ wave packet spectrum [Fig. 3(b)] exactly matches the calculated position of the 2-1 and the 2-2 Coulomb explosion channels. This strongly indicates that the observed spectra really originates from Coulomb explosion of a highly charged molecular ion rather than dissociation of some highly excited state into I and I^{2+} . A further proof of the Coulomb explosion mechanism comes from the fact that the wave packet motions are also observed in the I^{3+} signal. Again, the agreement with the calculated

positions of the photofragmentation channels (mainly 3-1 and 3-2) is very good.

At larger time delays the dispersion of the wave packets (see below) will eventually result in an overlap of the peaks from the different explosion channels. However, the limited resolution of our spectrometer at lower kinetic energies of the ejected ions is the main factor that prevents us from resolving the peaks for delay times greater than 3.7 ps. Also, the different fragmentation channels are not separated when the wave packet is evolving in the $^1\Pi_u^+$ potential [Fig. 3(a)] since the much faster wave packet motion results in large internuclear distances (low kinetic energies of the fragments) even at short time delays.

Figure 3 also shows TOF spectra obtained at a time delay of 100 ps where the internuclear distances are so large that the kinetic energy of the ionic fragments is determined almost solely by the dissociation velocity of the wave packet [Eqs. (1) and (2)]. Here, the $^1\Pi_u^+$ and $B^3\Pi_u^+$ wave packets show up as two sets of peaks separated by ~ 74 and ~ 23 ns, respectively (see Fig. 3). Thus, these spectra are a clear manifestation of the two different dissociation channels. The limited resolution of the spectrometer gives rise to the observed broadening toward lower kinetic energies and to the appearance of the central peak in the upper trace of Fig. 3(a). This peak results from molecules excited to the B state aligned perpendicular to the TOF axis since the dissociation velocity of the B -state wave packet is so low that many of the ionic fragments pass through the apertures in the spectrometer.

We now discuss the dispersion of the wave packets and the temporal extent of the peaks in Fig. 3. In general, the width of the wave packet increases with time due to the different propagation velocities induced by the different frequency components of the exciting laser pulse and by initial thermal population of vibrational states. The width

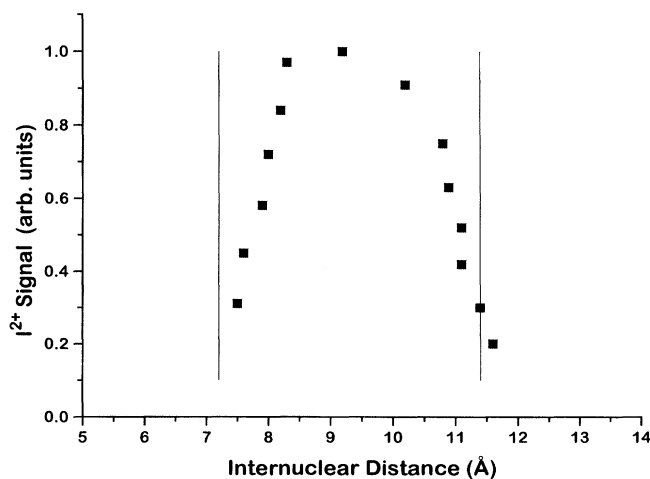


FIG. 4. The dimension of the B -state wave packet measured after 1.0 ps. The vertical lines indicate the calculated extent of the wave packet (see text).

of the wave packets can be determined from the TOF spectra by using Eq. (2). This is illustrated in Fig. 4 for the *B*-state wave packet at a time delay of 1.0 ps based on a point-wise deconvolution of the (2-2) explosion channel (the $1/E_{\text{kin}}$ dependence of the collection efficiency is taken into account). The data fall virtually within the two vertical lines at 7.2 and 11.4 Å which mark the maximal extent of the wave packet structure after 1.0 ps expected for excitation with a 300 fs long laser pulse of 10 nm bandwidth ($\sim 425 \text{ cm}^{-1}$) and for initial population of the $v = 0, 1, 2$ vibrational levels in the ground state of I_2 (Boltzmann distribution at room temperature).

Now that we can directly measure wave packet structure it is important to consider the resolution limit. A fundamental limit is given by the final de Broglie wavelength of the exploding ions. At an internuclear separation of $\sim 10 \text{ Å}$ and for the (2-2) fragmentation channel this limit is very small indeed ($< 0.02 \text{ Å}$). A more severe limit is imposed by the pulse duration τ of the probe laser. Nuclei move during the pulse and this motion leads to an uncertainty in the position when ionization takes place given by $\sim v_{\text{WP}}\tau$. Thus, for $R \geq 6 \text{ Å}$, features as small as 0.5 Å should be resolvable for the *B*-state wave packet in this experiment.

With minor improvements in the resolution of our spectrometer the Coulomb explosion technique should allow us to follow the temporal evolution of the dimension of the wave packet over a large range of internuclear distances as well as to study more complex time dependent shapes of the wave packets. For example, Krause *et al.* [15] have suggested focusing a dissociative wave packet launched in the I_2 *B* state to form a narrow distribution of the internuclear separation centered at a chosen position by exciting the wave packet by a short laser pulse with a substantial positive chirp. Building on this ability to manipulate wave packets, Coulomb explosion from well characterized wave packets opens an approach for determining the potential curves of highly charged molecular ions. Furthermore, the proposal for strong field-induced explosive ionization at critical internuclear distances [16] and strong field bonding [17] is now available for experimental investigation.

In summary, we have introduced a new technique to measure the dynamics of nuclear molecular wave packets. The method is based on Coulomb explosion induced by intense fs laser irradiation and subsequent recording of

the kinetic energy of the ionic fragments. As a first demonstration, the technique was applied to measure the motion of two different dissociative wave packets in I_2 . Particularly important is that the technique can be used to determine the dimension of wave packets. It will now be possible to measure the general shapes of wave packets. Finally, the prospects of using the Coulomb explosion method in spectroscopic studies as well as to investigate strong field phenomena, were pointed out.

It is a pleasure to acknowledge the important contribution from P. Dietrich in the initial phase of this work as well as technical support from D. Joines and discussions with A. D. Bandrauk and many of our colleagues at NRC. E. C. wishes to thank the International Council for Canadian Studies for financial support.

-
- [1] A. H. Zewail, Faraday Disc. Chem. Soc. **91**, 207 (1991).
 - [2] L. D. Noordam, A. ten Wolde, and H. B. van Linden van den Heuvell, in *Laser Interactions with Atoms, Solids and Plasmas*, edited by R. M. More, NATO ASI, Ser. B, Vol. 327 (Plenum Press, New York, 1994).
 - [3] T. Baumert *et al.*, Phys. Rev. Lett. **69**, 1512 (1992); H. Hohmann *et al.*, *ibid.* **73**, 1919 (1994).
 - [4] P. Kowalczyk, C. Radzewicz, J. Mostowski, and I. A. Walmsley, Phys. Rev. A **42**, 5622 (1990).
 - [5] T. J. Dunn, J. N. Sweetser, I. A. Walmsley, and C. Radzewicz, Phys. Rev. Lett. **70**, 3388 (1993).
 - [6] C. Meier and V. Engel, J. Chem. Phys. **101**, 2673 (1994).
 - [7] I. Fischer, D. M. Villeneuve, M. J. J. Vrakking, and A. Stolow, J. Chem. Phys. (to be published).
 - [8] J. P. Bergsma *et al.*, J. Chem. Phys. **84**, 6151 (1986).
 - [9] J. C. Williamson and A. H. Zewail, J. Phys. Chem. **98**, 2766 (1994).
 - [10] Z. Vager, R. Naaman, and E. P. Kanter, Science **244**, 426 (1989).
 - [11] C. Rölland and P. B. Corkum, Opt. Commun. **59**, 64 (1986).
 - [12] P. Dietrich, D. T. Strickland, M. Laberge, and P. B. Corkum, Phys. Rev. A **47**, 2305 (1993).
 - [13] R. J. Oldman, R. K. Sander, and K. R. Wilson, J. Chem. Phys. **54**, 4127 (1971).
 - [14] R. J. Leroy, J. Chem. Phys. **52**, 2678 (1970).
 - [15] J. L. Krause, *et al.*, J. Chem. Phys. **99**, 6562 (1993).
 - [16] M. Ivanov, T. Seideman, and P. B. Corkum (unpublished).
 - [17] M. Schmidt, D. Normand, and C. Cornaggia, Phys. Rev. A **50**, 5037 (1994).