Steering a molecule into dissociation via vibrational excitation

Alexander Kästner¹, Frank Grossmann¹,⁴, Sebastian Krause¹, Rüdiger Schmidt¹, Anatole Kenfack² and Jan-Michael Rost³

¹ Institut für Theoretische Physik, Technische Universität Dresden, 01062 Dresden, Germany
² Physikalische und Theoretische Chemie, Institut für Chemie und Biochemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin, Germany
³ Max Planck Institute for the Physics of Complex Systems, Nöthnitzer Strasse 38, 01187 Dresden, Germany
E-mail: frank@physik.tu-dresden.de

New Journal of Physics 11 (2009) 083014 (7pp)
Received 12 May 2009
Published 13 August 2009
Online at http://www.njp.org/
doi:10.1088/1367-2630/11/8/083014

Abstract. For a laser driven molecule, we show that the ionization and the dissociation channels can be separated by preparing the molecule in a specific vibrational state. Specifically, we investigate the dynamics of the hydrogen molecular ion under a femtosecond infrared laser field aligned with the molecular axis. We find dissociation probabilities of more than 60%, considerably higher than reported so far. We demonstrate that a full dimensional description of the electron dynamics is necessary to obtain accurate results for the combined ionization/dissociation dynamics.

Recent intriguing theoretical results have revealed that electron localization during molecular dissociation of the hydrogen molecular ion by pulsed laser excitation can be controlled by using the carrier envelope phase [¹], leading to maximal dissociation probabilities slightly above 20%. The competing process of ionization has to be kept at a minimum to achieve this goal experimentally, however [²]. Also, with monochromatic laser light, achieving dissociation is a relatively difficult task [³]. Consequently, high intensity is required for dissociation, for instance, $I \approx 10^{13}$ W cm$^{-2}$ for a hetero-nuclear diatomic like HF [⁴]. Even in the case of half cycle pulse fields, which have a very broad frequency content, intensities $I > 10^{13}$ W cm$^{-2}$ are required to achieve on the order of 15% dissociation probability [⁵]. At such high intensities,
the ionization process dominates and masks vibrational excitation and dissociation. Chelkowski et al [6] therefore suggested that the dissociation threshold of a diatomic molecule can be lowered by two orders of magnitude using a down-chirped laser, tracing the decrease in spacing of the excited energies levels. This pathway of dissociation does not work for a homo-nuclear diatom like the hydrogen molecular ion, which does not have a permanent dipole moment in the electronic ground state. Following a different path, namely stochastic driving of small quantum systems [7, 8], it has been shown recently that in this way dissociation of about 30% can be reached for H$_2^+$ starting from the ground state [9].

Apart from investigations starting from a specific initial state [10]–[12], also a systematic study regarding the influence of the initial vibrational excitation $\nu$ on the dissociation probability has been published with a maximal probability of about 30% [13] in a one-dimensional description. In our investigation detailed below, we find a dissociation probability of more than 60% for a molecule that is aligned with the linearly polarized laser field, using a time-dependent, full quantum approach. The discrepancy originates in the different modeling used. The sensitivity of dissociation to approximations in the theoretical description is not surprising since the degree of dissociation is the result of a delicate interplay between nuclear and electronic dynamics. We have studied the aligned molecular configuration to provide a fair comparison with the previous one-dimensional results [13]. Moreover, we can treat the problem fully quantum mechanically since the aligned molecule requires only three degrees of freedom (see below). The results agree well with those obtained from our quantum–classical mixed approach. This is important since—in contrast to the full quantum solution—the mixed approach can easily be used for rotating molecules that require a higher dimensional configuration space.

Related work on the dependence of time-dependent photodissociation on vibrational excitation has been performed in a two-level approximation with and without the rotating wave approximation [15]. In this early work, however, due to the restriction to just two electronic levels, the effect of ionization has not been included. As the experimental realization of state selective experiments with H$_2^+$ is starting to become possible [16, 17], it is important to deliver precise theoretical predictions of what is to be expected if a hydrogen molecular ion, prepared in a specific initial vibrational state, is irradiated with an infrared laser pulse.

As stated before we investigate the hydrogen molecular ion under the influence of a laser pulse that is polarized along the molecular axis. This leads to cylindrical symmetry of the problem and therefore three degrees of freedom (two for the electron and one for the nuclei) are sufficient for a full description. Thus, we solve the time-dependent Schrödinger equation for the hydrogen molecular ion in a linearly polarized laser field numerically, eliminating the center of mass motion and assuming that the nuclei are restricted to move along the laser polarization vector [10]. Adding a dipole-coupled laser field $E(t)$, the time-dependent Schrödinger equation in atomic units is given by

$$i \frac{\partial}{\partial t} \Psi(z, \rho, R, t) = \left[ T_{\text{vib}} + T_e + V + z \kappa E(t) \right] \Psi(z, \rho, R, t),$$

with the kinetic energy $T_{\text{vib}} = -M^{-1}_p \frac{\partial^2}{\partial R^2}$ of the protons, the electronic kinetic energy$^5$

$$T_e = -\frac{1}{2\mu_e} \frac{\partial^2}{\partial z^2} - \frac{1}{2\mu_e} \left[ \frac{\partial^2}{\partial \rho^2} - \frac{1}{\rho} \frac{\partial}{\partial \rho} \right],$$

$^5$ We would like to point out that there is a misprint of the kinetic energy in equation (8) of [9].

New Journal of Physics 11 (2009) 083014 (http://www.njp.org/)
and the potential energy

\[ V(\rho, z, R) = -[\rho^2 + (z - R/2)^2]^{-1/2} - [\rho^2 + (z + R/2)^2]^{-1/2} + 1/R, \]

where \(1/\mu_e = 1 + 1/(2M_p)\), \(\kappa = 1 + 1/(2M_p + 1)\), \(M_p\) is the proton mass in units of the electron mass, \(R\) is the internuclear distance, and \(z\) and \(\rho\) are cylindrical coordinates of the electron. The laser field we chose is identical to the one used by Feuerstein and Thumm \[13\] with 800 nm wavelength and a full-width at half-maximum (FWHM) of 25 fs, leading to a total duration of 50 fs of the laser pulse. The maximum intensity is \(I = 2 \times 10^{14} \text{ W cm}^{-2}\).

Due to the cylindrical symmetry of the driven system an expansion of the wavefunction in a Bessel–Fourier series in \(\rho\) is performed. The singularity of the Coulomb potential is retained, without any softening of the potential and we treat the electronic motion in full 3d. The time-dependent Schrödinger equation (1) can then be solved by the standard split operator FFT technique \[18\]. We start the propagation by using the ground electronic state times an excited nuclear wavefunction as initial state \(\Psi(\rho, z, R, t = 0)\). The calculation of the initial state was performed by first calculating the electronic ground state wavefunction by imaginary time propagation. With the potential energy surface for the nuclei \[19\], their time-independent Schrödinger equation was solved by discretizing the second derivative and diagonalizing the Hamilton matrix numerically and thereby determining the vibronic eigenstates. We note in passing that we checked that without the external field, the system will stay in the product initial state indefinitely, i.e. the non-Born Oppenheimer coupling with higher electronic states is negligible.

The observables we will display and discuss in the following are the ionization probability

\[ P_I(t) = 1 - \int_0^{R_{\text{max}}} f_1(R, t) dR \]  

and the dissociation probability that is defined without ionization according to

\[ P_D(t) = \int_{R_0}^{R_{\text{max}}} f_1(R, t) dR. \]

Here, \(f_1\) is obtained by integrating \(|\Psi(\rho, z, R, t)|^2\) over electronic coordinates inside a cylinder of radius \(\rho_0 = 8 \text{ a.u.}\) and height \(2 \times z_1\). The nuclear separation defining the onset of dissociation into the H + H\(^+\) channel is taken as \(R_D = 9.5 \text{ a.u.}\) as in \[10\]. We have checked that the asymptotic results for the probabilities to be presented below do not depend on that specific choice. The quantity \(f_1\) is explicitly given by

\[ f_1(R, t) = 2\pi \int_{-z_1}^{z_1} dz \int_0^{\rho_0} d\rho \rho |\psi(R, z, \rho, t)|^2 \]

and defined slightly differently as compared to \[9\]. There we had included a broadening of the cylinder with increasing \(R\) as displayed in figure 3 of \[9\]. Qualitatively, the results reported below would not change, however. The differences are on the order of below 1%.

In our full quantum calculations, the electronic grid for \(z\) contains 1024 points and extends from \(-50 \text{ a.u.}\) to \(50 \text{ a.u.}\). The time step is equal to 0.01 a.u. = \(2.4 \times 10^{-4} \text{ fs}\). Furthermore, a quadratic imaginary potential has been used to avoid unphysical reflections at the electronic grid boundaries. The onset of ionization is defined to be at \(z_1 = 25 \text{ a.u.}\). The nuclear grid consists
of 512 points, extending from $R_{\text{min}} = 0.38$ a.u. to $R_{\text{max}} = 30$ a.u. and 16 basis functions were used in the Bessel–Fourier expansion for $\rho$. We have checked that decreasing the left boundary of the nuclear grid by a factor of two does not change the results to be presented in the following. Furthermore, increasing the number of Bessel functions to 20 does also not change the results as does the increase of the maximal cylinder radius to $\rho_0 = 10$ a.u.

For reasons of comparison, we also performed alternative quantum–classical calculations based on the so-called non-adiabatic quantum molecular dynamics (NA-QMD) theory [20]. In this approach, the motion of the nuclei is treated classically and the dynamics of the electrons is treated quantum mechanically using time-dependent density functional theory in basis expansion in the general, i.e. multielectron case. Recently the NA-QMD has been extended to realistically describe also ionization processes by introducing absorbing boundary conditions in basis expansion [21]. As in previous applications of the NA-QMD to the hydrogen molecule [22] and molecular ion [23], we are using here a localized Gaussian basis expansion, in order to describe accurately both ionization and dissociation. The initial conditions for the vibrationally excited nuclei were chosen according to a classical distribution with energies given by the correct quantum eigenvalues of the vibrational states [24]. A total of around 200 trajectories was enough to converge the results to within a few per cent relative accuracy. Due to the ultra-short pulsed laser that is employed here, we have used the standard NA-QMD without the possibility to separate different channels (i.e. without electron–nuclear correlations [25]). All details of the calculations (basis expansion, absorbing boundary conditions, classical initial conditions, classical calculations of the probabilities (4) and (5), etc) can be found in [21, 23].

We first present full quantum results for the ionization probability $P_I(t)$ and the dissociation probability $P_D(t)$ as a function of time for a selected set of initial vibrational excitations in figure 1. As can be seen from the figure, shortly after the pulse is over (after around 75 fs), asymptotic values for $P_I$ and $P_D$ are reached.
Figure 2. (a) Full quantum results for ionization and dissociation (without ionization) probabilities after excitation with a 25 fs laser as a function of the initial vibrational states \(v = 0, \ldots, 14\) for \(\text{H}_2^+\). (b) NA-QMD results for the same laser parameters.

In figure 2, the asymptotic results \(P_I(\infty)\) and \(P_D(\infty)\) are shown as a function of initial vibrational excitation. The upper panel shows the full quantum results and the lower one the NA-QMD ones. Firstly, for low \(v\), the sum of ionization and dissociation probability is considerably smaller than unity, indicating that part of the wavefunction stays bound. Secondly, in both panels an increase in the ionization probability with increasing initial excitation is observed, while for \(v \geq 9\) the ionization probability slightly decreases again. We observe dissociation probabilities as high as 60% for the initial excitations \(v = 1, 2\). These are to the best of our knowledge the highest values that have been reported so far. The result is promising due to the fact that the experimental realization of our results would require vibrationally excited \(\text{H}_2^+\), which is typically prepared by tunneling ionization of \(\text{H}_2\), leading to predominant excitation of levels \(v \leq 4\) [17]. Furthermore, it is very remarkable that the quantum–classical results displayed in the lower panel of figure 2 show not only a qualitative but also a quantitative similarity with the full quantum calculations for almost all vibrational quantum numbers except for \(v = 0\) where the quantum–classical dissociation probability is definitely zero and the exact quantum calculation predicts a probability of about 6%. On the other hand, in both approaches the dissociation probability increases rapidly when \(v\) becomes larger than 0, indicating resonant behavior for \(v \geq 1\) and non-resonant conditions for \(v = 0\). Therefore the vanishing dissociation probability for \(v = 0\) is very likely due to the use of classical initial conditions in the nuclear motion.

The chosen laser parameters are by no means unique or exceptional. In order to prove this we have run the same calculations for a laser pulse of half the length as compared to the one above but with the same maximal amplitude. The results for the dissociation as well as ionization probabilities are displayed in figure 3. Here the dissociation starts to increase more slowly with the initial vibrational excitation, but it finally acquires even higher values, larger than 60% again for relatively low values of \(v = 2, 3, 4\) (full quantum). The ionization is still increasing even for \(v = 13\). It is, however, on an appreciably lower level of around 40% due to
the fact that the energy content of the pulse is less than that underlying the results displayed in figure 2. We stress that the ionization and dissociation probabilities show a qualitatively different behavior in figure 3 as compared to figure 2. Whereas for the long pulse, ionization overtakes dissociation for large ν, in figure 3 the opposite is true (except for large vibrational excitation ν ≥ 11 in the full quantum case). In both cases the overall predictive power of the NA-QMD results is surprisingly good.

In summary, using a full quantum description for the H₂⁺ molecule aligned in a linearly polarized laser field, we have found dissociation probabilities of more than 60%, which to our knowledge is the largest value reported so far, even though other theoretical studies have used laser intensities five times as high [1]. For even longer pulse lengths and the same intensity as considered herein, the ionization is expected to increase due to the effect of charge resonance enhanced ionization [26]. The lower dissociation probabilities reported in [13] for the 25 fs pulse have led us to the conclusion that the one-dimensional model for H₂⁺ with soft-core Coulomb potentials [14] is too restrictive to obtain realistic dissociation probabilities. Finally, our results are corroborated by a quantum–classical study, which shows surprisingly similar results, except for the lowest vibrational initial state. Since the quantum–classical treatment can be easily applied for more degrees of freedom, it suggests itself as a promising approach to describe even rotating molecules in strong laser fields adequately.

Acknowledgments

We thank Jan Handt for useful discussions and help with the NA-QMD calculations. AK acknowledges useful discussions with I Barth and A D Bandrauk.

References

[1] Roudnev V, Esry B D and Ben-Itzhak I 2004 Phys. Rev. Lett. 93 163601
[2] Kling M F et al 2006 Science 312 246
[3] Blömbergen N and Zewail A H 1984 J. Chem. Phys. 88 5459

*New Journal of Physics* 11 (2009) 083014 (http://www.njp.org/)
[4] Chelkowski S and Bandrauk A D 1990 Phys. Rev. A 41 6480
[5] Lin J T, Lin S H and Jiang T F 2000 Phys. Rev. A 61 033407
[6] Chelkowski S, Bandrauk A D and Corkum P B 1990 Phys. Rev. Lett. 65 2355
[7] Kenfack A and Rost J M 2005 J. Chem. Phys. 123 204322
[8] Singh K P and Rost J M 2007 Phys. Rev. Lett. 98 160201
[9] Kenfack A, Rost J M and Grossmann F 2008 New J. Phys. 10 013020
[10] Chelkowski S, Zuo T, Atabek O and Bandrauk A D 1995 Phys. Rev. A 52 2977
[11] Posthumus J H 2004 Rep. Prog. Phys. 67 623
[12] Paramonov G K 2005 Chem. Phys. Lett. 411 350
[13] Feuerstein B and Thumm U 2003 Phys. Rev. A 67 043405
[14] Kulander K C, Mies F H and Schäfer K J 1996 Phys. Rev. A 53 2562
[15] Bandrauk A D, Aubanel E E and Gauthier J M 1994 Molecules in Laser Fields ed A D Bandrauk (New York: Dekker) chapter 3, pp 109–79
[16] Sändig K, Figger H and Hänisch T W 2000 Phys. Rev. Lett. 85 4876–9
[17] Urbain X, Fabre B, Staicu-Casagrande E, de Ruette N, Andrianarijaona V M, Jureta J, Posthumus J H, Saenz A, Baldit E and Cornaggia C 2004 Phys. Rev. Lett. 92 163004
[18] Feit M D, Fleck J A and Steiger A 1983 J. Comput. Phys. 47 412
[19] Wind H 1965 J. Chem. Phys. 42 2371
[20] Kunert T and Schmidt R 2003 Eur. Phys. J. D 25 15–24
[21] Uhlmann M, Kunert T and Schmidt R 2006 J. Phys. B: At. Mol. Opt. Phys. 39 2989
[22] Uhlmann M, Kunert T and Schmidt R 2005 Phys. Rev. A 72 045402
[23] Uhlmann M, Kunert T, Grossmann F and Schmidt R 2003 Phys. Rev. A 67 013413
[24] Wind H 1965 J. Chem. Phys. 43 2956
[25] Uhlmann M, Grossmann F, Kunert T and Schmidt R 2007 Phys. Lett. A 364 417
[26] Chelkowski S, Conjusteau A, Zuo T and Bandrauk A D 1996 Phys. Rev. A 54 3235