

Vibrational Excitation of Diatomic Molecular Ions in Strong Field Ionization of Diatomic Molecules

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A model based on the strong-field and Born-Oppenheimer approximations qualitatively describes the distribution over vibrational states formed in a diatomic molecular ion following ionization of the neutral molecule by intense laser pulses. Good agreement is found with a recent experiment [X. Urbain *et al.*, Phys. Rev. Lett. **92**, 163004 (2004)]. In particular, the observed deviation from a Franck-Condon-like distribution is reproduced. Additionally, we demonstrate control of the vibrational distribution by a variation of the peak intensity or a change of frequency of the laser pulse.

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Intense investigations during the last decades have led to quite a detailed understanding of the interaction between strong laser fields and atoms (see [1] for a review). This includes, e.g., the process of high-harmonic generation which is by now a valuable source for the production of coherent ultraviolet light. For molecules, however, the extra degrees of freedom introduced by the presence of more than one nucleus lead to a much more involved picture, and the description of the strong-field driving of such systems far from equilibrium is still a challenge in theoretical physics (for reviews, see [2,3]).

The main topic of this work is to investigate the partitioning of energy among the electronic and nuclear degrees of freedom when ionizing a diatomic molecule by a strong laser field. This is a topic of much current interest: until recently it was assumed that the distribution over vibrational states formed in the molecular ion following ionization of the neutral molecule follows a Franck-Condon (FC) distribution, and this assumption is still frequently used (see [4] and references therein). A recent experiment, however, reported a non-FC distribution and suggested that the use of the FC principle is inaccurate because the rate for tunneling ionization increases sharply with internuclear distance [4]. We will show that the rapid response of the electron to the laser field in fact ensures the applicability of the FC principle for the nuclear motion at each instant of time during the pulse. It is instead the variation of the ionization and excitation rate with intensity in the focal volume that leads to a departure from a conventional FC-like distribution. The theory is very versatile and readily adapted to a wide range of diatomic molecules.

We note that as the strong-field response of the molecular ion is very dependent on the distribution over vibrational levels, it is desirable to be able to control the latter. We show by explicit examples in H_2 , O_2 , and N_2 that a simple change of the peak intensity of a 45 fs Gaussian pulse leads to a significant degree of control over the final vibrational distribution, and hence holds the promise for the production of a target of interest for state-specific studies.

The energy absorbed by a molecule in the field is distributed among the electrons and nuclei. Ionization of molecules is accordingly accompanied by a vibrational excitation of the nuclear motion in the ion formed. To illustrate the accuracy of our approach, we first consider H_2 for which strong-field experiments are available [4–6]. For H_2 both photoelectron spectroscopy with UV light sources [7] and ionization by 100 eV electron impact [4] resulted in vibrational distributions of H_2^+ in accordance with the FC principle, i.e., governed by the projection of the initial vibrational ground state wave function $\nu' = 0$ onto the set of vibrational states of the molecular ion, ν . In recent experiments [4–6], the vibrational distribution of H_2^+ was measured after ionization of H_2 by intense laser fields. These experiments revealed very different vibrational distributions than the experiments mentioned above. The laser-induced ionization leads to a narrower distribution with almost no population in the final vibrational levels above $\nu = 4$, and the actual shape of the distribution depends on the peak laser intensity and wavelength. At low intensities, the maximum population is observed in the $\nu = 0$ state while the FC principle predicts a maximum population in the $\nu = 2$ state. These results can be partly reproduced by a tunneling model with an electronic binding energy which depends on the internuclear distance [4–6]. However, the experimental conditions in some of the experiments [6] do not correspond to a pure tunneling regime, and a further shortcoming of the model is that it cannot account for any variation in the distribution with wavelength. It is therefore desirable to apply a theory that is expected to be valid also in the multiphoton regime. An example of such a theory is the molecular strong-field approximation with the inclusion of nuclear motion [8–10], and here we apply this theory along the lines discussed in [10]. This model has previously reproduced various experimental observations quite successfully [10,11]. For a linearly polarized laser of frequency ω and periodicity $T = 2\pi/\omega$, the rate of ionization differential in the direction \hat{q} of the ejected electron, to a particular vibrational state of the molecular ion after absorption of n photons is

$dW_{fi}/d\hat{q} = 2\pi|A_{fi}|^2q_n$ (atomic units, $e = \hbar = m_e = a_0 = 1$, are used throughout). The magnitude of the momentum q_n is determined by energy conservation and A_{fi} is the transition amplitude,

$$A_{fi} = S_{fi} \frac{1}{T} \int_0^T \langle f(t) | V_F(t) | i(t) \rangle dt, \quad (1)$$

where S_{fi} is the FC factor corresponding to the nuclear vibrational transition, $V_F(t)$ is the length gauge form for the molecule-light interaction, and $|i(t)\rangle$ and $|f(t)\rangle$ are the initial and final electronic states, respectively, including energy phases for the nuclear vibrational motion. The time scale of molecular rotations is much slower than the typical pulse duration so that the molecular orientation is considered as being fixed throughout the pulse. The time scale of the vibrational motion, on the other hand, is shorter than the typical pulse length and therefore we treat this degree of freedom quantum mechanically. The initial electronic state is the highest occupied molecular orbital, and in the final state it is assumed that the laser-electron interaction is much stronger than the electron-molecule interaction, such that the final state of the electron can be accurately described by a Volkov wave. In Eq. (1), the electronic matrix element is evaluated at the equilibrium distance of the nuclei in accordance with the Born-Oppenheimer approximation. This allows us to isolate the overlap between the nuclear wave functions expressed by the FC factor. Under experimental conditions, the temperature will be sufficiently low so that only the vibrational ground state of the initial state is populated. We integrate over all directions of the outgoing electron and sum over all accessible numbers of photon absorptions to obtain the total rate of ionization to the vibrational state considered. Finally, and this turns out to be essential, we integrate the total rates over the Gaussian spatial and temporal profile of the laser pulse and average over molecular orientations for direct comparison with experimental data. The spatial integration is carried out over the interaction region which is restricted to a small volume around the beam waist in the experiment. It is not difficult to show that relative signals are independent of focal spot size.

In Fig. 1, we present the experimental and theoretical vibrational distribution of H_2^+ produced by strong-field ionization of H_2 for two different intensities. For comparison also squared FC factors are shown. At both intensities, we find good agreement between experiment and theory. Both distributions favor the lower vibrational states in contrast to the FC distribution.

Our aim is to provide a widely applicable model and therefore we simply use the field-free FC factors. These are readily available in the literature for a wide range of molecules. In reality, the field-free nuclear potential curves are distorted by a very intense laser field; e.g., in H_2^+ this effect leads to a bond softening due to a coupling between the lowest Σ_g and Σ_u states. As the potential is changed, a

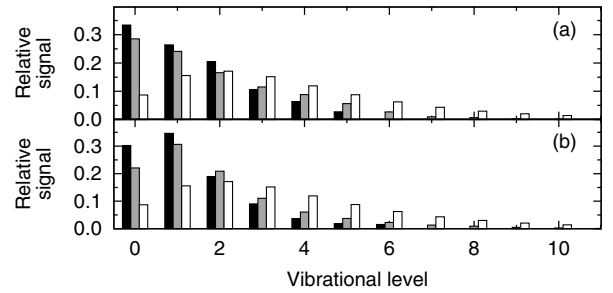


FIG. 1. The vibrational distribution of H_2^+ after ionization in an intense laser field. The black bars indicate the experimental observations [4] and the gray bars are the predictions according to the present theory. The Franck-Condon distribution is indicated with white bars. In both panels the laser wavelength is 800 nm; the pulse duration (full width at half maximum) is 45 fs. The peak laser intensities are (a) 3.0×10^{13} W/cm² and (b) 4.8×10^{13} W/cm².

new set of vibrational eigenstates and corresponding FC factors needs to be considered. If, however, the intensity is below 5×10^{13} W/cm² the field-induced modification of the potential curve is minimal [4] and the application of the field-free FC factors accurate. Also, we note that dissociating channels become increasingly important as the intensity exceeds 5×10^{13} W/cm², and since one might be interested in making subsequent experiments on the *bound* molecular ion we will not consider such intensities here.

Even though the FC principle is explicitly used in our theory [see Eq. (1)], the predicted and observed vibrational distributions deviate significantly from the FC distribution. The key concept explaining this discrepancy is the effect of channel closings in connection with full account of the pulse profile. By energy consideration, the number of absorbed photons n must fulfil the criterion $n\omega = q_n^2/2 + I_p^\nu + U_p$ with $q_n > 0$, I_p^ν the ionization potential to the level ν , and $U_p = I/(4\omega^2)$ the quiver energy of a free electron in the laser field of intensity I . The presence of U_p means that the minimum number of photons needed to reach the electronic continuum and a particular vibrational state ν in the ion increases with intensity. This phenomenon is referred to as channel closing and the effect is illustrated in Fig. 2, where we show the ionization rates to the lowest vibrational levels of H_2^+ when ionizing molecules aligned parallel to the laser field at a wavelength of 800 nm. At an intensity of 1×10^{13} W/cm² all the vibrational states shown can be reached by absorption of 11 photons. As the intensity increases the thresholds shift upwards by U_p and at the intensities marked by arrows, absorption of 11 photons becomes insufficient to reach the vibrational levels indicated. For example, in the intensity range of 2.3 – 2.7×10^{13} W/cm² one needs $n \geq 12$ photons to reach the $\nu \geq 1$ levels whereas $n = 11$ is sufficient for $\nu = 0$. Since the rates for higher order processes ($n \geq 12$) are much lower than the rate for $n = 11$, this explains why the $\nu = 0$ is favored by a factor of 3 over $\nu = \{1, 2\}$.

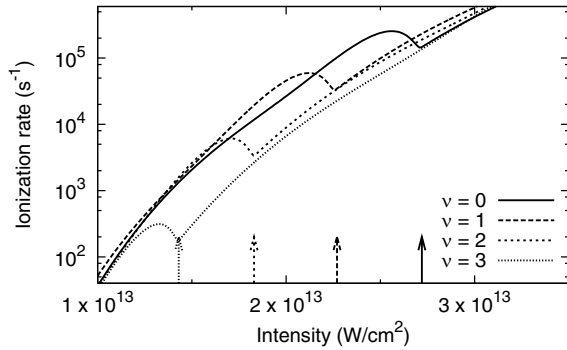


FIG. 2. Ionization rates to the lowest vibrational states of H_2^+ from H_2 molecules aligned parallel to the laser field at the wavelength of 800 nm. Note logarithmic scale.

On the contrary, when the same number of photons is needed to reach all ν levels, the rate to $\nu = 0$ is generally lower than to $\nu = \{1, 2\}$ due to the smaller FC factor of the former.

The reason for finding a very different relative relationship between the *signals* at the peak intensity of $3 \times 10^{13} \text{ W/cm}^2$, Fig. 1(a), and the *rates* at the same intensity is a result of taking the pulse shape into account. Only in the very center of the Gaussian laser beam the intensity reaches the peak intensity. In other regions of space the molecules are exposed to a lower intensity and excitation to $\nu = 0$ dominates.

So far we have seen that the vibrational distribution depends markedly on the intensity. Our next purpose is to investigate how the properties of the laser pulse can be varied to maximize the population in a given vibrational state. A high degree of population transfer to a definite state will be a valuable result as it will allow for the possibility of making state-specific experiments on the molecular ion. To our knowledge, such type of control has not previously been explored in strong-field physics. We have chosen to model the pulse by a simple variation of the peak intensity with the purpose of maximizing the $\nu = 0$ population. We have performed the optimization at the wavelengths corresponding to the fundamental- and frequency-doubled wavelengths of the Ti:sapphire (400 nm and 800 nm) and Nd:YAG (532 nm and 1064 nm) lasers. During optimization, the pulse duration is fixed at 45 fs and 6 ns for the Ti:sapphire and Nd:YAG wavelengths, respectively.

The result of the intensity optimization is shown in Fig. 3. At the shortest wavelength, 400 nm, a relative population as large as 75% is produced in the vibrational ground state at an intensity of $2 \times 10^{12} \text{ W/cm}^2$. At lower intensities we can get nearly 100% in the $\nu = 0$ state but at such low intensities the ion yields are very low. In our model, the reason for obtaining such a confined distribution is that the ion yield is completely dominated by 5-photon absorption which is only possible to the $\nu = 0$ state and only at intensities below $4.9 \times 10^{12} \text{ W/cm}^2$. We note

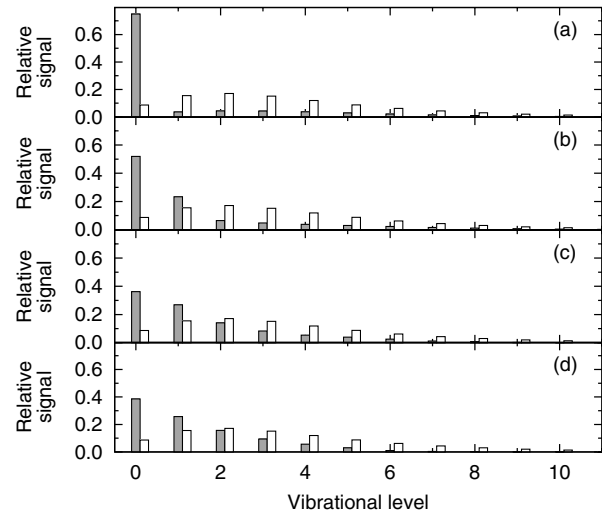


FIG. 3. The vibrational distribution of H_2^+ after ionization in an intense laser field according to the present theory (gray bars). The Franck-Condon distribution is indicated with white bars. The peak laser intensity is chosen to maximize the population in the lowest vibrational state. The laser wavelengths are (a) 400 nm, (b) 532 nm, (c) 800 nm, and (d) 1064 nm, and the peak intensities are (a) $2.0 \times 10^{12} \text{ W/cm}^2$, (b) $2.7 \times 10^{13} \text{ W/cm}^2$, (c) $2.6 \times 10^{13} \text{ W/cm}^2$, and (d) $1.9 \times 10^{13} \text{ W/cm}^2$. The pulse duration is 45 fs in panels (a) and (c), and 6 ns in panels (b) and (d).

that this explanation of the favoring of the $\nu = 0$ level is different from a previous suggestion offering an explanation in terms of resonance enhanced ionization [6]. As the wavelength increases the selection of the $\nu = 0$ becomes less efficient. At all wavelengths the optimum intensity is relatively low and it will always correspond to an intensity which is slightly below the occurrence of the first channel closing. The decreasing $\nu = 0$ population with increasing wavelength was also observed experimentally [5,6], and the general phenomenon that the largest population in the vibrational ground state is obtained at relatively low intensities is in good agreement with the experiments.

We note that the control obtained by changing intensity and/or wavelength is not only the simplest way of gaining control, it is probably also the only one. If, e.g., one considers the possibility of coherent control by preparing either a coherent superposition of initial vibrational states separated by the energy of one photon or by utilizing a bichromatic field and optimizing the strengths and relative phase of the two components of the field, one faces the problem of a continuum of final states. With a proper choice of amplitudes and phase it is possible to exclude the transition to one particular final state which is characterized by the vibrational state *and* the direction and energy of the outgoing electron. However, one cannot gain control over the transition to all other final states and hence an efficient selection cannot be made.

The vibrational wave functions of H_2 and H_2^+ lead to a quite broad FC distribution and accordingly many vibra-

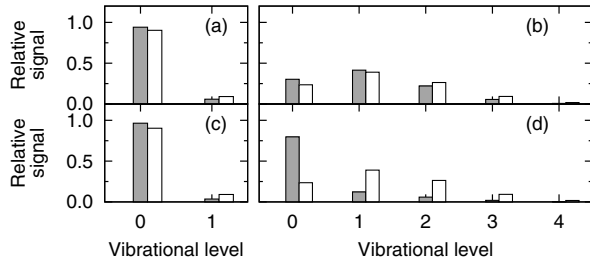


FIG. 4. The vibrational distribution of N_2^+ [(a) and (c)] and O_2^+ [(b) and (d)] after ionization in an intense laser field according to the present theory (gray bars). The Franck-Condon distributions are indicated with white bars. In all panels the laser wavelength is 800 nm and the pulse duration is 45 fs. A typical peak intensity of 5×10^{13} W/cm² is chosen in panels (a) and (b). Maximization of the population in the lowest vibrational state is obtained with the peak intensities of (c) 2.4×10^{13} W/cm² for N_2^+ and (d) 3.6×10^{12} W/cm² for O_2^+ .

tional states are populated after ionization. If one considers molecules where only a few FC factors are important, one may hope for a more efficient optimization. To this end, and to illustrate the wide applicability of the present formalism, we investigated ionization of N_2 and O_2 where the number of final vibrational states are limited to $\nu \leq 1$ and 4, respectively, simply because the other FC factors are vanishingly small. First, we calculated the vibrational distribution with a laser wavelength of 800 nm, pulse duration of 45 fs, and with a typical, but arbitrarily chosen, peak intensity of 5×10^{13} W/cm². We then made an optimization similar to that for H_2 and the results are given in Fig. 4. The vibrational distributions obtained with a typical peak intensity, Figs. 4(a) and 4(b), are quite similar to the FC distributions. Figure 4(a) shows typical and Fig. 4(c) optimized vibrational distribution of N_2^+ after ionization of N_2 . For N_2 , only two states will be populated in N_2^+ and we see that the FC factors strongly favor the $\nu = 0$ state (90%). By utilizing a nonoptimized strong laser field we obtain a $\nu = 0$ population of 94% [Fig. 4(a)], and if we use an optimized laser intensity we may reach a $\nu = 0$ population of 97% [Fig. 4(c)]. In Figs. 4(b) and 4(d) we present the results for O_2 and we see that an efficient selection of the $\nu = 0$ state can also be obtained for this molecule. We find the optimal population to be 80% [Fig. 4(d)] compared with the FC distribution of 24% and the nonoptimized result of 30% [Fig. 4(b)]. When we compare the results of N_2 and O_2 with the results of H_2 at the same wavelength

[Fig. 3(c)], we see that the former molecules can indeed be brought to the $\nu = 0$ state more efficiently due to the limited number of final vibrational states.

In conclusion, the molecular strong-field approximation with the inclusion of nuclear vibrational motion explains the recently observed vibrational distributions of H_2^+ produced by strong-field ionization of H_2 molecules [4]. The theoretical and experimental distributions are both very different from distributions predicted by Franck-Condon factors—a result that can be explained by the effects of channel closings in association with the spatial and temporal extend of the laser pulse. The theory is simple to evaluate and therefore readily applicable to diatomic molecules. We proposed a readily available method of optimizing the population in the $\nu = 0$ state by varying the peak laser intensity. With this type of optimization we showed that the vibrational distributions vary significantly with the laser wavelength in accordance with experimental findings. Finally, we applied the theory to N_2 and O_2 and found that a higher degree of control can be obtained than in H_2 due to the FC factors which are nonvanishing for fewer states in the former cases. We note that efficient control of population distributions will be of great value in the development of state-specific experiments on molecular ions.

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