Laser-Intensity Dependent Vibrational Excitation and Alignment of Molecular Ions in the Ultrafast Multiphoton Regime

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(Received 7 October 2008; published 5 December 2008)

H_2 molecules were ionized in the ultrafast ($\sim$150 fs) multiphoton regime (263 nm, $\sim 10^{13}$ W cm^{-2}). Earlier experiments investigated the kinetic energies of electrons or ions only. Using a unique experiment, we show that the vibrational excitation of molecular ions contains essential information about the dynamics of the process. In addition, we prove some earlier interpretations wrong. A realistic model based on vibronically excited intermediates, Stark shifting into resonance, reproduces the measurements, demonstrating that resonances continue to be important in the femtosecond regime. This eventually enables ultrafast control of the vibrational excitation of molecular ions, which is relevant to the whole field of molecular physics and physical chemistry.

The standard experimental methods for studying the interaction of ultrafast lasers with gases involve the investigation of photon spectra (mainly of higher harmonics) and the kinetic energies of electrons and ions (recoil ions and ions originating from dissociative-ionization and Coulomb-explosion events). For atoms this combination of spectroscopies appears sufficient, since multiphoton ionization (MPI) by ultrafast lasers rarely populates electronically excited states [1]. For molecules, on the other hand, the additional degrees of freedom complicate the physics substantially [2]. For example, in the simplest case of molecular multiphoton ionization, i.e., $H_2 + mh\nu \rightarrow H_2^+ + e^-$, the excess energy will not only transfer into kinetic energy of the electron and recoil energy of the ion but also into rovibrational excitation of the H_2^+ ion, which has no dipole and will therefore not radiate. So is it necessary to investigate the excitation of H_2^+ further?

One might object that, because of conservation of energy and momentum, high-resolution electron spectroscopy should suffice. It turns out that this is correct for MPI with nanosecond lasers [3] but not for subpicosecond lasers and much higher intensities [4,5] for this reason: Immediately after ionization, the electron is in the intense laser field. Its kinetic energy is the sum of translational kinetic energy and the oscillatory ponderomotive energy. Subpicosecond pulses, however, turn off faster than the electron can leave the focus, and so the ponderomotive energy flows back to the laser field [6]. Since the lost energy is easily larger than the vibrational level spacing, electron spectroscopy gives little information on the excitation of the molecular ion. A second objection might be that further photon absorption will open the dissociative-ionization ($H + H^+ + e^-$) and Coulomb-explosion ($H^+ + H^+ + 2e^-$) channels. However, a correct interpretation of the kinetic energy releases (KERs) and angular distribu-

tions of these nonlinear processes without an independent examination of the H_2^+ vibrational excitation is very difficult.

Concerning MPI, it is necessary to distinguish between the tunneling regime and the multiphoton regime [7], the latter being less understood and the subject of the present work. Previously, we showed that the tunneling regime yields H_2^+ ions with the population concentrated in $v^+ < 5$ vibrational levels [8]. This was very different from the broad Franck-Condon (FC) distribution that had incorrectly been taken for granted for approximately 10 years [9]. The explanation was a very strong dependence of the tunneling rate on the internuclear distance R [8,10].

In the theoretically more challenging multiphoton regime, experimental photoelectron spectra indicate that resonances with Rydberg levels play an important role [4,5]. The process might therefore be related to resonance-enhanced multiphoton ionization (REMPI), which is well known for much longer and less intense laser pulses [3]. The electron spectra, however, do not allow us to pinpoint the vibrational levels inducing the resonances, nor do they reveal which vibrational levels in H_2^+ are populated [5]. Likewise, the dissociative-ionization and Coulomb-explosion experiments in the multiphoton regime were difficult to interpret. Although the present results are consistent with the previous experimental results, we reject the earlier interpretations [11,12], as discussed below.

There are also good practical reasons for studying the vibrational excitation of molecular ions after MPI in the multiphoton regime. With laser pulses shorter than the rotational period of the molecules, the alignment of the molecular axis is practically frozen during the interaction. Alignment-selective ionization enables preparing the alignment of the molecular ions. This type of control has

already sparked very interesting experiments [13]. The present work further demonstrates that it is possible to prepare the vibrational excitation of H_2^+ [14].

For the determination of the vibrational excitation of H_2^+ formed in the multiphoton regime, we used a unique setup (coined here "reaction endoscope") developed at Louvain-la-Neuve. The operational principle of the reaction endoscope was detailed in [8]. In brief, the H_2^+ ions, with their unknown vibrational excitation, are extracted from the focus by an electric field and accelerated to 2 keV. Here the ions pass an effusive jet of potassium atoms. The charge exchange with the H_2^+ ions is well understood [15]. One of the reaction products is an excited triplet state of H_2. The short-lived triplet state couples to a repulsive state, and thus the H_2 molecules predissociate to two neutral H atoms, which are subsequently measured in coincidence on two position sensitive detectors. Positions and arrival times enable us to calculate the KER of the dissociation event, which reveals the vibrational excitation of the H_2 triplet state before predissociation. This in turn is related to the vibrational excitation of the H_2^+ ions before the charge exchange. The FC matrix describing the relationship is approximately diagonal for the lower vibrational levels. The resolution of the reaction endoscope is 90 meV FWHM, sufficient to easily resolve the vibrational structure but insufficient to resolve the rotational structure.

In our choice of laser source, we have to ensure to be well inside the multiphoton regime [7]. This limits our choice of wavelength to the UV. Concerning pulse duration, shorter than several picoseconds suffices for the short-pulse regime. Nevertheless, in order to induce ponderomotive shifts larger than the vibrational level spacings, the pulses should be considerably shorter than 1 ps. Only then is the saturation intensity (at which the MPI probability approaches unity) well above 10^{13} W cm^{-2}. The saturation intensity sets an upper limit on the useful laser intensity and therefore on the ponderomotive shift. A frequency-tripled amplified Ti:sapphire laser meets the criteria. Its wavelength also largely avoids resonances with the B state. The reaction endoscope was therefore moved to the CEA Saclay Laser-Matter Interaction Center, where a Ti:sapphire laser (45 fs, 800 nm, 600 μJ at 1 kHz) was frequency tripled and used for MPI of H_2. The center laser wavelength at the third harmonic was 263 nm, the bandwidth was 4 nm, and the pulse duration was approximately 150 fs. Two different spherical lenses were used for focusing the 7 mm diameter beam: one of $f = 300$ mm for the three lowest intensities and one of $f = 70$ mm for the five highest intensities. In the subsequent experiment, we observed a small discrepancy between the ac-Stark shifts of the Rydberg states and the calculated ponderomotive shifts, which could be removed by multiplying the estimated intensities by a factor of 0.6. Since this is within experimental uncertainty, and since we expect the just-mentioned shifts to be equal [16], we decided to use the rescaled laser intensities, which together range from 3.2×10^{12} to just above 10^{14} W cm^{-2}.

Figures 1(a) and 1(b) show two experimental spectra corrected for the KER-dependent angular acceptance. The spectra are rich in detail and vary substantially as a function of laser intensity. Clearly, the vibrational excitation of the molecular ions contains a large amount of information which is not observed by other types of spectroscopy [4,5,11,12]. Figures 1(c) and 1(d) show modeled spectra that will be detailed later. The KER spectra consist of 19 peaks at fixed positions in the range 7.3–10.2 eV, corresponding one to one to the vibrational levels of the H_2 triplet state formed in the K jet. Taking into account the FC matrix, we extracted the ν^+ populations of H_2^+ by least-square fitting 90-meV-wide Gaussian-like curves to the peaks. The populations are shown on the map in Fig. 2(a). The smooth evolution of the populations with laser intensity justified a linear interpolation along the Y coordinate. The saturation intensity is approximately 8×10^{13} W cm^{-2}, and we are therefore not showing the one measurement above this intensity. Figures 2(b) and 2(c) show modeling results. The Gaussian profiles along the X coordinate ease comparison with Fig. 1. The four dotted lines correspond to the spectra of Fig. 1. We note that there is a matrix transformation between the data of Figs. 1 and 2. The data underlying Fig. 2 can be obtained from the authors on request.

The theoretical treatment of MPI of molecules is still very challenging, and so it uses, for example, the recently introduced molecular strong-field approximation [17]. Neglecting intermediate resonances, it predicts relatively simple vibrational level distributions in H_2^+, reminiscent of the tunneling regime [8]. Our experiments demonstrate the opposite: complex distributions apparently related to excited states of H_2. Other theoretical approaches include electronic intermediates but merely predict ionization rates, not vibrational excitation [18]. Thus, not being able
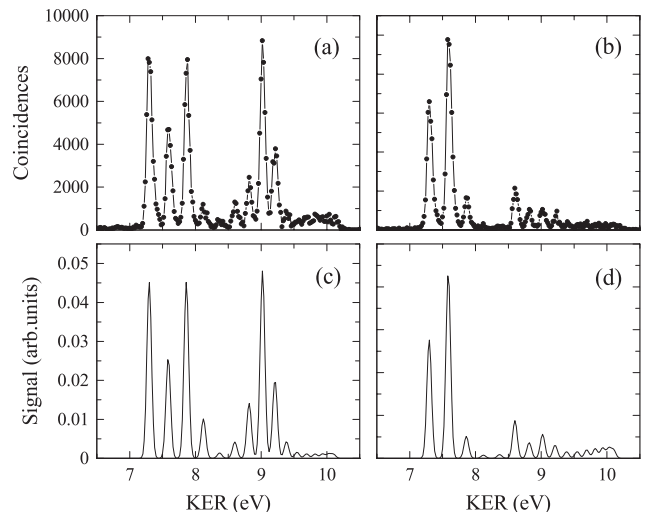

FIG. 1. Experimental KER spectra at (a) $I = 1.5 \times 10^{13}$ W cm^{-2} and (b) $I = 5.4 \times 10^{13}$ W cm^{-2}. (c),(d) Modeled spectra at intensities corresponding to (a) and (b).
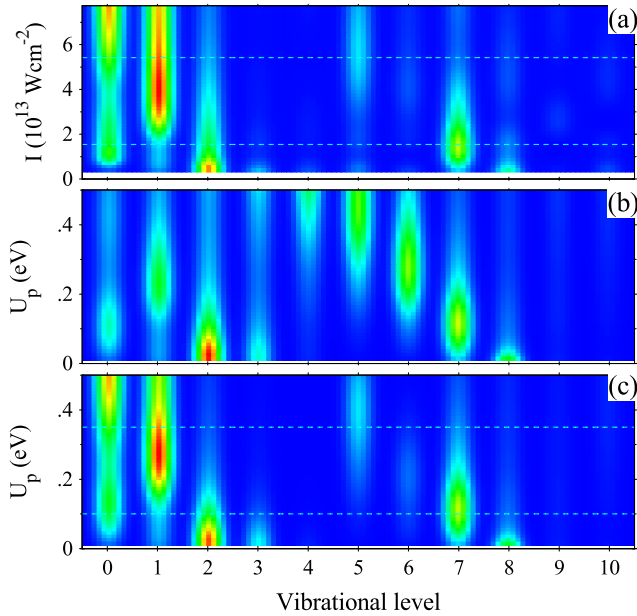
FIG. 2 (color online). (a) Experimental relative populations of $v^+ = 0$–10 of H_2^+ produced by MPI of H_2 at 263 nm. (b) Results of a model based on REMPI with ponderomotive shifts of resonances. (c) Including photodissociation of H_2^+. Dashed lines refer to Fig. 1 (see text).

to compare with *ab initio* theory, we interpret the spectra with a REMPI-like model adapted to subpicosecond, high intensity laser pulses. Beginning with a qualitative understanding of the data, we turn to Fig. 3. The absorption of three photons corresponds to an excitation energy of 14.13 eV, as indicated. The unperturbed potential curves of the four lowest ungerade states [19] are drawn as well. Concerning the D state, the excitation energy is in between $v = 0$ and 1 implying there is no resonance at low intensity. When the laser intensity increases, the levels shift upwards. The $v = 0$ initially shifts into resonance and
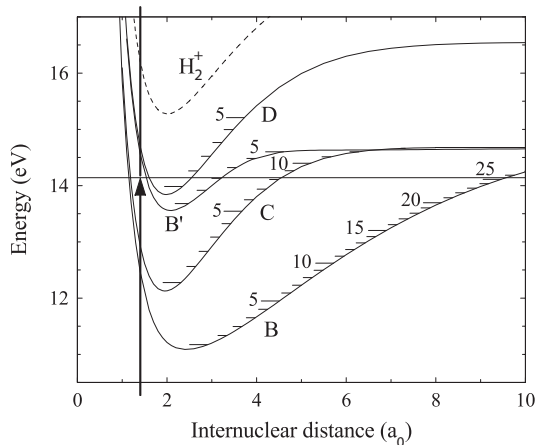

FIG. 3. Potential-energy diagram showing the four relevant excited states of H_2 [19] and the ground state of H_2^+. The states are $B\ ^1\Sigma_u^+$, $C\ ^1\Pi_u$, $B'\ ^1\Sigma_u^+$, and $D\ ^1\Pi_u$.

then shifts out again. For the B', C, and B states, the first resonances are at $v = 2$, 8, and 25, respectively, and then shift to lower v's for increasing intensity. The vibrational quantum numbers are virtually conserved for ionization of the D, B', and C states, because their potential curves are almost parallel to that of H_2^+ and the FC matrices are therefore nearly diagonal for the lower v's. The high v's of the B state, on the other hand, transfer to a broad range of high levels of H_2^+, observed here as a row of small populations at the right-hand side of the spectra in Fig. 1. Because of the poor overlap with the bound levels of H_2^+, the high B levels may also ionize directly to the $H + H^+$ continuum [20], yielding near-zero-energy H^+ previously assigned to zero-photon dissociation [11].

The quantitative model operates in three steps: population of vibrational levels of H_2 excited states, subsequent ionization, and finally partial photodissociation. $Q(1)$ and $P(1)$ transitions are assumed for Π_u and $^1\Sigma_u^+$ resonances, respectively, $J = 1$ being the most populated rotational level of H_2 at room temperature. For the first step, the populations are calculated as the product of three factors: (i) the relative strength of the 3-photon electronic transitions, (ii) the FC overlap between the H_2 ground state and the resonant level, and (iii) the resonance condition, i.e., the overlap between a Gaussian centered at the excitation energy and a Lorentzian centered at the level of the Stark-shifted resonance. We assume that the ac-Stark shifts are equal to the ponderomotive shift [16], i.e., to $0.93\lambda^2 I$ [eV], where I is the intensity in units of $10^{13}\ \mathrm{W\,cm^{-2}}$ in the focus of a linearly polarized laser beam and λ is the laser wavelength in microns. The width of the Gaussian corresponds to a laser bandwidth of 4 nm times $\sqrt{3}$ (for three photons). The width of the Lorentzian corresponds to the lifetime of the resonance and varies linearly with laser intensity due to photoionization. For our model, we assume a photoionization cross section of 10^{-18} cm^2 for all resonances. This value corresponds to Kramers' formula for hydrogenlike systems, with $N = 3$. For simplicity, the electronic transition strengths are assumed independent of R and were given the values 0.4, 1, 3.2, and 5 for the D, B', C, and B states, respectively. For optimal agreement between calculations and measurement, the unperturbed potential curves of the C and D states were moved slightly upwards by 80 and 40 meV, respectively, while the unperturbed B' curve was moved a little downwards by 40 meV, effectively shifting the population somewhat towards lower or higher v's. The reason for these shifts may be a strong R dependence of the electronic transition strengths, as observed for tunneling ionization [8]. Also, the generation of rotational wave packets (e.g., pendular states) is a possible explanation [13].

The second step is ionization of the excited states. We assume that the populations are transferred to the v^+ levels of H_2^+ according to the FC overlaps. Here, too, we neglect a possible R dependence of the ionization rate. The results of the model so far are shown in Fig. 2(b).

As a last step, we include photodissociation of H_2^+. Photodissociation survival probabilities were calculated at an intensity of 3.5×10^{12} W cm^{-2} for molecules aligned parallel to the polarization with the help of time-dependent wave packet calculations and then scaled for the other intensities, considering exponential depletion proportional to the peak intensity. For otherwise aligned molecules, only the parallel component of polarization induces the photodissociation. This effectively reduces the "felt" laser intensity. Since the pulse duration is much shorter than the rotational period, molecules that are accidentally aligned approximately parallel preferably ionize via Σ resonances. These dissociate according to our calculations. Molecules with approximately perpendicular alignment ionize via Π resonances. The corresponding "perpendicular" H_2^+ molecules are more robust against photodissociation. We find good agreement with the experiment if the effective laser intensity for dissociation of H_2^+ populated through Π resonances is reduced by a factor of 3.6.

Earlier experiments on multiphoton dissociative ionization of H_2 at 266 nm are perfectly consistent with this interpretation [12]. The molecules with $v^+ = 2$ or lower, populated through a Σ resonance, are aligned approximately parallel to the laser polarization, giving rise to a sharply peaked "parallel" angular distribution of the $H + H^+$ channel. The $v^+ = 3$–8 levels, populated through a Π resonance, are approximately perpendicular aligned. Together with the dissociation probability which favors parallel aligned molecules, this results in a bone-shaped angular distribution, without requiring a torque to be exerted on vibrationally trapped states [12].

The result of the full model is shown in Fig. 2(c). Now the agreement with Fig. 2(a) is also quantitative. Finally, for the modeled spectra in Figs. 1(c) and 1(d), we multiply the calculated distributions with the appropriate FC matrix. Also, on this level of comparison the agreement is good. At the high intensities, the width of the resonances becomes larger than the vibrational level spacing. In this case the absorption of 3 photons launches vibrational wave packets on the potential curves of the resonant states. Subsequent ionization transfers the wave packets to H_2^+. The higher the intensity, the more the vibrational structure of the resonances loses its relevance, since the REMPI process becomes so fast that it occurs at approximately fixed R [18].

In conclusion, we determined the vibrational excitation of H_2^+ after ionization of H_2 in the multiphoton regime and found a complex distribution very different from both predictions using the molecular strong-field approximation and results in the tunneling regime. Nevertheless, we are able to reproduce the results with a model based on Stark-shifting resonances. We introduce relative 3-photon coupling strengths and ac-Stark shifts equal to the ponderomotive energy. Concerning photodissociation, we find that the molecular ions produced through Π resonances are relatively stable due to perpendicular alignment with respect to the laser polarization. The dissociation of these ions leads to bone-shaped angular distributions [12] which were interpreted incorrectly before, just as the near-zero-energy H^+ [11]. The final agreement between model and experiment is good, although certain aspects, e.g., the 3-photon coupling strengths, their R dependence, and the role of rotational wave packets, require further investigation. The present work clearly demonstrates the necessity of measuring the vibrational excitation of H_2^+ for a proper understanding of ultrafast MPI of H_2 in the multiphoton regime.

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