Franck–Condon factors for the ionization of hydrogen and deuterium molecules in laser fields

M. E. Sukharev

Moscow State Engineering Physics Institute, 115409 Moscow, Russia

V. P. Kraĭnov

Moscow Physico-Technical Institute, 141700 Dolgoprudnyĭ, Moscow Region, Russia

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Franck–Condon factors are calculated for the ionization of hydrogen and deuterium molecules in intense low-frequency laser fields. It is shown that the laser field shifts the maximum of the Franck–Condon factors towards higher ion excitation energies. In the strong-field case, the vibrational levels of molecular ions disappear and a continuous distribution of Franck–Condon factors is observed as a function of the vibrational excitation energy. © *1996 American Institute of Physics.* [S1063-7761(96)00409-X]

1. INTRODUCTION

The Franck–Condon factors for transitions between the ground vibrational state of a neutral molecule and the various excited vibrational states of the ion resulting from the ionization process, are especially important in the interpretation of many experiments on the interaction of laser radiation with simple molecules. These factors were calculated by Dunn (see Ref. 1) for molecules of hydrogen and deuterium in the Born–Oppenheimer approximation. Because the electronic and nuclear coordinates are separable, the motion of electrons can be discussed with the nuclei kept motionless at fixed distances from one another. This latter assumption, referred to as the Franck–Condon principle, states that the internuclear distance does not change during ionization of a neutral molecule. Then the probability of a vertical transition between the ground state of the molecule, described by the wave function $\varphi_0(R)$, and some excited state of the molecular ion with the corresponding wave function $\psi_E(R)$ has the form

$$W_E=\left|\int_0^\infty \varphi_0(R)\psi_E(R)dR\right|^2, \qquad (1)$$

where R is the internuclear distance and E is the energy of the molecular-ion state under discussion.

The energy of the molecular ion state is a more appropriate quantity to use than the vibrational quantum number, because intense low-frequency laser fields cause part or all of the discrete vibrational levels of the molecular ion to disappear, so that the system has only a continuous spectrum of nuclear states.

The wave functions defined above are calculated numerically, in accordance with the Born–Oppenheimer approximation, at the instant of time where the amplitude of the laser field is a maximum. Because the probability of tunneling ionization of a neutral molecule depends exponentially on the magnitude of the field, the most molecular ions are obtained from neutral molecules at the maximum field amplitude. Furthermore, in the majority of cases the axis of the molecule is directed along the field (for a linearly polarized field, the axis of the molecule is directed along the axis of polarization), because this orientation of the molecule leads to the maximum output of ions.

2. CALCULATIONS

The wave function of the ground vibtrational state of a hydrogen molecule (deuterium molecule) can be found from the one-dimensional Schrödinger equation:

$$\left(-\frac{1}{M}\frac{d^2}{dR^2}+V(R)-\frac{1}{2}FR\right)\varphi_0(R)=E_0\varphi_0(R). \qquad (2)$$

Here M is the mass of a proton (twice the proton mass for the case of the deuterium molecule), E_0 is the energy of the ground vibrational state of the molecule (it is worth noting that this state does not disappear at the fields under discussion in this paper), and F is the amplitude of the intense low-frequency laser radiation. Here and in what follows we use the atomic system of units:

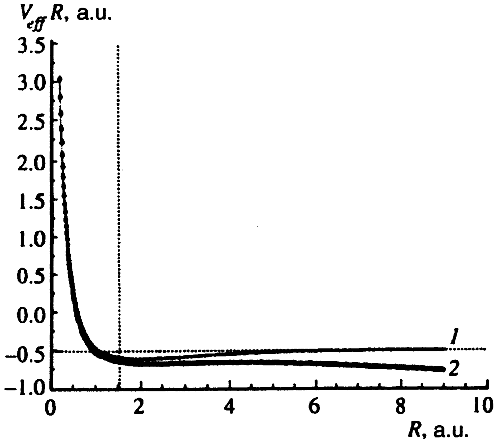

FIG. 1. Effective potential of a hydrogen molecular ion as a function of the distance between nuclei in a field $F=0$ (curve *1*) and in a field $F=3\cdot 10^8$ V/cm (curve *2*). The vertical dashed line denotes the Franck–Condon transition from the ground state of the neutral hydrogen molecule.

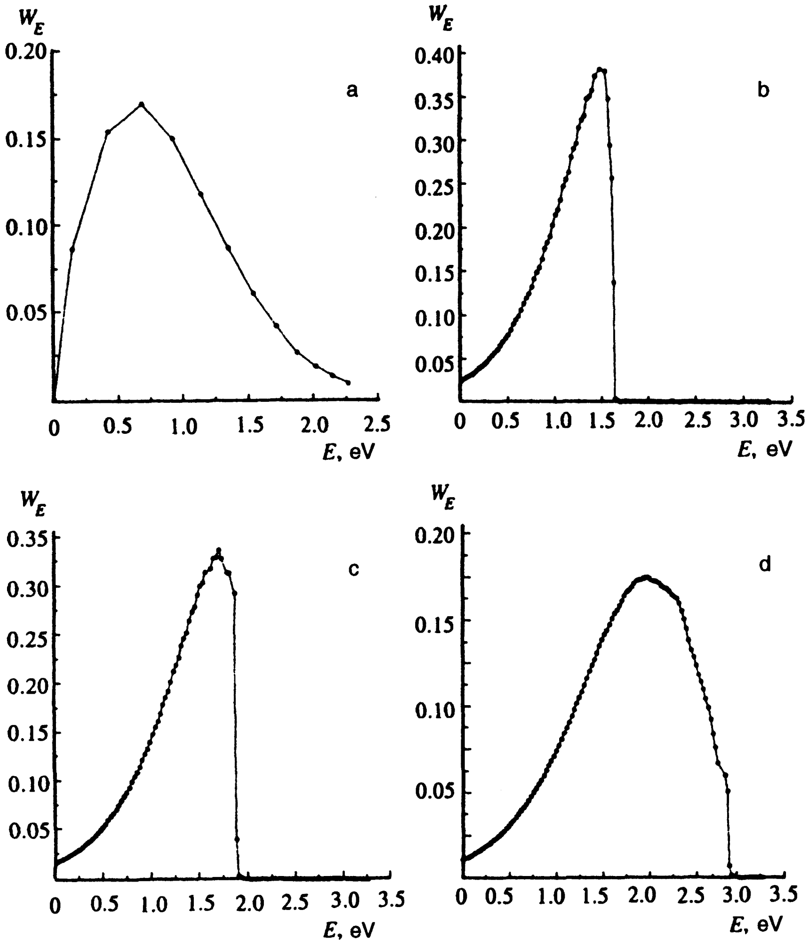

FIG. 2. Franck–Condon factors for hydrogen molecules as a function of the excitation energy E for various fields. The excitation energy E is given in eV, and $E=2.649$ eV corresponds to the potential for dissociation of the molecular ion. The Franck–Condon factors are normalized by using the relation $\int (W_E/\omega_e)dE=1$, where ω_e is the oscillator frequency of the lowest of the molecular ion states (in eV). $F=0$ (*a*), $5\cdot 10^7$ (*b*), 10^8 (*c*), and $3\cdot 10^8$ V/cm (*d*).

$$e=\hbar=m_e=1.$$

The potential $V(R)$ for a neutral molecule is chosen in the form (see Ref. 1)

$$V(R)=0.3493(e^{-2x}-2e^{-x})$$

for $R>0.727$, $x=1.0298(R-1.410)$ and

$$V(R)=\left(\frac{1}{R}-\frac{1}{0.727}\right)$$

for $R<0.727$. It is clear that $V(R)$ is described by a Morse function at large R and a Coulomb potential at small R.

The term that depends on field on the left side of (2) represents the dipole interaction of the molecule with the laser field, and the effective charge of the proton is taken to equal $e/2$ (of course, this is correct only at large internuclear distances; however, a more precise value of the effective charge can be introduced only for molecular ions, because the external field perturbs this ion more strongly than it does a molecule).

The vibrational states of the molecular ion and the wave functions are found from the following Schrödinger equation:

$$\left(-\frac{1}{M}\frac{d^2}{dR^2}+V_i(R)-\frac{1}{2}FRf(R)\right)\psi_E(R)=E\psi_E(R). \tag{3}$$

The effective charge of the proton $f(R)$ was computed by Il'kov[1)] using a two-level approximation (a detailed discussion of this problem can be found in Ref. 2). The potential $V_i(R)$ for a hydrogen molecular ion is taken from Ref. 3, where it was found numerically using the Schrödinger equation for an electron in the field of two protons. The use of this potential in the form taken from Ref. 3, and not in the form of a Morse function with known parameters, is dictated mostly by the fact that calculations based on the Morse function do not give correct results (see Ref. 1).

The energy E in (3) corresponds to a bound vibrational state when the field equals zero or is weak; for a strong field the energy E from (3) takes on a continuous spectrum.

The effective nuclear potential

$$V_{\text{eff}}(R)=V_i(R)-\frac{1}{2}FRf(R) \tag{4}$$

is shown in Fig. 1 for $F=3\cdot 10^8$ V/cm. It is clear that there are no bound vibrational states for such a field.

The potential (4) is fitted to a cubic polynomial on the interval (0.2 a.u., 5.0 a.u.) with a step size of 0.2 a.u., and on the interval (5.0 a.u., 9.0 a.u.) with a step size of 0.5 a.u., by using cubic spline interpolation as implemented in MAPLE 5 R.3. The eigenvalues of the Hamiltonian operator in (3), if there are any for this field, are computed by a variational method, after which computation of the corresponding wave

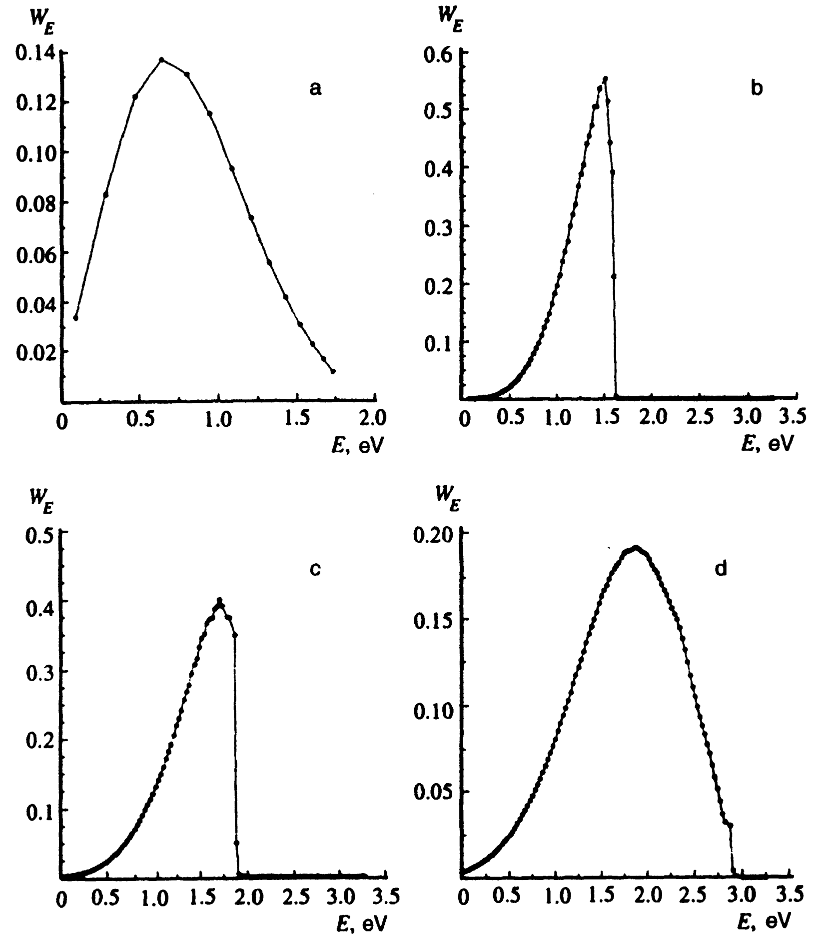

FIG. 3. Franck–Condon factors for deuterium molecules as a function of excitation energy for the same values of field and with the same normalization relation as in Fig. 2.

functions no longer requires very much effort. The wave functions obtained for the molecular ion and wave function of the ground vibrational state of the neutral molecule are given in the form of tables; then these wave functions, based on the program described above, are fitted to cubic polynomials on the interval (0.2 a.u., 9.0 a.u.) with the step size of 0.01 a.u.. Finally, the Franck–Condon factors are calculated in accordance with (1) based on the Gauss quadrature formula.

3. RESULTS AND CONCLUSION

If there is no laser field, the Franck–Condon factors calculated in this paper coincide with the results of Dunn[1] The results for hydrogen are given in Fig. 2, and in Fig. 3 for deuterium. It is clear that the vibrational states with quantum numbers $v=1-4$ for hydrogen and with $v=2-5$ for deuterium are more intensely excited when the field equals zero. For the fields used in the experiments of Chin's group,[4,5] the maximum in the Franck–Condon factors as a function of excitation energy should be shifted in the direction of higher energies.

The results of this paper can be used to advance the understanding of the processes of dissociation and ionization of molecular ions in intense low-frequency laser fields, and also to study the dynamics of molecular ions (see Ref. 6).

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[1)] F. A. Il'kov, private communication.

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