Double tunneling: An overlooked quantum effect in anionic molecular clusters

Pavel Jungwirth and Vladimír Špirko

J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 18223 Prague 8, Czech Republic

Abstract

Simultaneous tunneling of an electron and nuclei in hydrogen bonded molecular clusters which support a dipole bound electron is reported. A whole class of systems including hydrogen halide and water dimer anions is predicted to exhibit this effect. A measurable signature of double tunneling is a strong reduction of the tunneling splitting compared to the neutral cluster. Quantum mechanical calculations give for the hydrogen fluoride dimer anion a ground state tunneling splitting of 114 MHz, while for the first excited vibrational state the tunneling splitting reaches 4.20 GHz.

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Tunneling is one of the most fascinating manifestations of quantum mechanics. While a classical object cannot overcome a barrier the height of which is larger than its energy, its quantum analogue has a non-zero probability to tunnel through the barrier. In molecular systems, particles for which this phenomenon is observed are primarily electrons and light atoms such as hydrogen. Electron tunneling can play an important role in electron transfer reactions [1] and it constitutes the working mechanism of scanning tunneling microscopy [2] or of tunneling microelectronic devices [3]. Nuclear (primarily hydrogen) tunneling is observed in many hydrogen-bonded systems such as the condensed phases and clusters of water or hydrogen halides [4–7]. To the best of our knowledge, no cluster system in which two vastly different species - electron and nuclei, simultaneously tunnel has been described so far. In this work, double tunneling is predicted to be present in a whole class of hydrogen-bonded molecular clusters supporting an excess electron. By double tunneling we mean a rearrangement of an anionic molecular system, where the nuclear tunneling between two equivalent minima on the Born-Oppenheimer potential energy surface is accompanied by tunneling of the excess electron between the two moieties of the cluster. We show, that a strong reduction of the tunneling splitting compared to the corresponding neutral dimer is a measurable fingerprint of double tunneling in hydrogen-bonded dimer anions. In the rest of the paper we quantify this prediction for the hydrogen fluoride dimer anion using high accuracy quantum chemical calculations followed by a numerical solution of the vibrational problem. At the end we discuss the results and their relevance for similar systems such as water cluster anions.

A significant effort has been recently directed to elucidation of the structure, binding and dynamics of an excess electron in a polar medium - the so called solvated or 'wet' electron [8–10]. A natural laboratory for performing high resolution spectroscopic experiments as well as accurate calculations are the corresponding finite size molecular clusters. While in large clusters the electron binding energy approaches its bulk value (typically around 1 eV), in small hydrogen-bonded clusters the electron is much more loosely bound [11–17]. As a rule, in the limit of a single polar molecule such as water, ammonia, or a hydrogen halide the electron is not bound at all and the smallest system which supports an excess electron is the corresponding dimer. This dipole bound electron remains well separated from the electronic structure of the neutral dimer and can be viewed as a separate quantum particle. It is very diffuse and is located at the positive end of the cluster dipole, i.e. close to the dangling hydrogen(s). Due to a weak excess electron binding, the structure of the neutral dimer changes only moderately upon electron attachment [17].

Tunneling in neutral hydrogen-bonded dimers is a well known phenomenon confirmed both by terahertz spectroscopy and quantum calculations e.g., for water and hydrogen fluoride dimers [7,18–25]. What happens, however, with the tunneling process if an excess electron is attached to these dimers? Since the electron binds to the dangling hydrogen(s), tunneling motions involving a hydrogen bond donor-acceptor interchange must be strongly affected. The donor-acceptor interchange is a switch in which a former dangling hydrogen becomes hydrogen-bonded while the old hydrogen bond breaks and a new dangling hydrogen emerges at the other side of the cluster (see ball and stick structures in Fig. 1). At the same time the orientation of the cluster dipole reverts. Therefore, the excess electron is forced to move to the other side of the dimer in concert with the nuclear tunneling motion. For symmetry reasons, the intermediate cluster geometry (middle structure in Fig. 1) has no dipole moment. As a result, it is not favorable for electron binding and represents a barrier not only for the nuclear motion but also for that of the excess electron. Neither the excess electron in its ground electronic state nor the nuclei in their ground or low-lying excited vibrational states have enough energy to *classically* overcome the barrier, however, both can and indeed do *quantally* tunnel through the barrier.

In the present paper, we demonstrate the quantum phenomenon of double tunneling on the case of the hydrogen fluoride dimer anion. This typical cluster with a dipole bound electron has been observed experimentally only very recently [14]. As a matter of fact, much more attention has been paid to its neutral precursor - the hydrogen fluoride dimer. Numerous experimental [19–21] and theoretical [22–28] studies have been devoted to elucidation of the structure and energetics of this system. A high quality potential energy surfaces exist for the neutral dimer [27,28] and vibrational calculations in full dimensionality have been performed providing spectroscopic data in a very good agreement with experiment [22].

Our knowledge of the dimer anion is much less spectacular. Recent experimental [14] and theoretical [16] studies have concentrated primarily on the minimum on the potential surface and on evaluation of vertical and adiabatic electron detachment energies. Possibly, this is the reason why the effect of double tunneling, the description of which requires knowledge of the electron-dimer interaction for a whole set of cluster geometries, has escaped attention so far. A rigorous description of the concerted nuclear and electron tunneling based on a fully dynamical treatment of both species would require an accurate electron-molecule interaction pseudopotential. Pseudopotentials do exist e.g., for the electron-water system and play an important role in large cluster and condensed phase studies [11]. However, they are certainly not accurate enough to describe the weak interaction between the neutral dimer and the dipole bound electron [17]. Fortunately, at least for the ground and low-lying vibrational and rotational states of the dimer, the Born-Oppenheimer approximation holds very well due to the big hydrogen/electron mass ratio and the fact that the weak binding of the excess electron is still larger than the energy of atomic motions. Therefore, one can safely use accurate methods of quantum chemistry for the investigation of double tunneling in the lowest vibrational and rotational states.

Recently, it has been shown that high level *ab initio* methods are required for the description of a dipole bound electron [16,17]. A sufficiently large and diffuse basis set is necessary to capture the very diffuse nature of the excess electron. Also, due to a huge polarizability of the loosely bound electron correlation effects play an important role and have to be included properly. In a recent study, it has been convincingly demonstrated that the Coupled Cluster method with single and double excitations including perturbative triples with an augmented correlation corrected double zeta basis with additional diffuse *sp* sets on the dangling hydrogen gives practically converged results for a set of dipole bound anions including $(HF)_2^-$, which are in a very good agreement with experiment [16]. Therefore, we have used this method and basis set for an extensive scan of the $(HF)_2^-$ potential energy surface [29].

Potentials and structures along the tunneling coordinate [24], which is a minimum energy path connecting the two equivalent minima of $(HF)_2^-$ via a corresponding saddle point, are shown in Fig. 1. Larger and smaller balls depict the fluorine and hydrogen atoms and the isosurfaces represent the orbital occupied by the excess electron. The full line is the anionic potential and the dashed line the neutral potential along the tunneling coordinate. The difference between the two potentials is the electron binding energy (dotted line).

Fig. 1 demonstrates that in the equilibrium geometry the diffuse excess electron is bound primarily to the dangling hydrogen. On the other hand, the symmetric transition structure with a zero dipole moment does not support an extra electron. Therefore, the anionic and neutral curves coincide in the saddle region. The potential curves exhibit a symmetric double well structure typical for the tunneling effect. Moreover, neither the excess electron in its ground state nor the nuclei with zero or small vibrational excitations have enough energy to classically overcome the barrier, therefore, both of them simultaneously tunnel. The tunneling motion of the electron and nuclei has to be concerted otherwise the potential would loose its symmetric double well shape. Indeed, if the excess electron moves alone to the other side of the cluster or the nuclei perform the donor-acceptor interchange without repositioning the electron, energy would monotonously rise and the effective potentials would exhibit only a single minimum.

A measurable signature of tunneling is the corresponding splitting of energy levels. The one-dimensional potential profiles along the tunneling coordinate (see Fig. 1) give a very good qualitative insight into the processes and one can immediately conclude that tunneling must be suppressed in the anion compared to the neutral cluster due to a deeper potential well. For accurate quantitative predictions of the splittings we have performed a two-dimensional calculation coupling explicitly the two H-F-F angular motions. The rest of the geometry parameters of the cluster remain practically constant during tunneling motions in low-lying vibrational states and can be treated as decoupled [23,24]. Fig. 2 depicts the two-dimensional potential energy surface of $(HF)_2^-$ as a function of the two H-F-F angles. It can be seen that these two angles change simultaneously during the tunneling process. The tunneling coordinate is roughly a part of a circle on the two-dimensional plot.

The tunneling splittings for low-lying vibrational states of $(HF)_2^-$ and $(HF)_2$, calculated similarly as in Ref. 24, are presented in Table I. The ground state tunneling splitting of the neutral dimer is 22.4 GHz ($\hat{=}$ 0.0917 meV). This value is in a good agreement both with experiment and with calculations in full dimensionality [22], which justifies the two-dimensional approximation. More importantly, the tunneling splitting drops by two orders of magnitude for the anion, being now equal to 114 MHz. The same effect occurs for the first vibrationally excited state in the tunneling coordinate, where the tunneling splitting drops from 482 GHz to 4.20 GHz. The strong decrease of the tunneling splitting when passing from neutral to anionic clusters is a measurable fingerprint of double tunneling. The fact that the splitting in the anion is smaller does not mean that it is experimentally less accessible. As a matter of fact, the opposite might well be true. The first excited state splitting shifts from a spectroscopically difficult far-infrared region into that of microwaves, which is covered by standard techniques, while the ground state anionic tunneling splitting falls into radiofrequencies. Other possible experimental routes for observing double tunneling are the zero electron kinetic energy (ZEKE) and double resonance photodetachment spectroscopies.

Double tunneling, i.e. simultaneous tunneling of an electron and nuclei, is by no means limited to $(HF)_2^-$ for which the first calculations have been performed. All hydrogen bonded dimers capable to support a dipole bound electron are predicted to exhibit this quantum phenomenon. The most important example of such systems is certainly the water dimer anion for which calculations are currently being performed. Another interesting issue concerns double tunneling for highly excited vibrational states of the dimer where the Born-Oppenheimer approximation fails and the excess electron has to be treated as a fully dynamical particle. However, questions concerning non-adiabatic couplings between the nuclear motion and that of the dipole bound electron can only be addressed once a reliable electron-dimer pseudopotential becomes available.

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REFERENCES

[1] J. Jortner and M. Bixon, Eds., *Electron transfer - from isolated molecules to biomolecules* (Wiley, New York, 1999), Adv. Chem. Phys. vol. 106-107.

[2] C. Bai, *Scanning tunneling microscopy and its application* (Springer, Berlin, 1995), Springer series in surface sciences vol. 32.

[3] I. Mehdi, R. K. Mains, G. I. Haddag, U. K. Reddy, Surf. Sci. **228**, 426 (1990).

[4] F. Bruni, G. Consolini, G. Careri, J. Chem. Phys. **99**, 538 (1993).

[5] R. J. Saykally and N. Pugliano, Science **257**, 1937 (1992).

[6] K. Liu, M. G. Brown, J. D. Crutzan, R. J. Saykally, Science *271*, 62 (1996).

[7] E. Zwart, J. Muelen, W. L. Meerts, L. H. Coudert, J. Mol. Struct. **147**, 27 (1991).

[8] K. Yokoyama, C. Silva, D. H. Son, P. K. Walhout, P. F. Barbara, J. Phys. Chem. A **102**, 6957 (1998).

[9] A. A. Mosyak, O. V. Prezhdo, P. J. Rossky, J. Chem. Phys. **109**, 6390 (1998).

[10] A. A. Mosyak, P. Graf, I. Benjamin, A. Nitzan, J. Phys. Chem. A **101**, 429 (1997).

[11] R. N. Barnett, U. Landman, A. Nitzan, J. Chem. Phys. **89**, 2242 (1988).

[12] P. Ayote and M. A. Johnson, J. Chem. Phys. **106**, 811 (1997).

[13] J. Kim, I. Becker, O. Cheshnovsky, M. A. Johnson, Chem. Phys. Lett. **297**, 90 (1998).

[14] J. H. Hendricks, H. L. de Clercq, S. A. Lyapustina, K. H. Bowen, Jr., J. Chem. Phys. **107**, 2962 (1997).

[15] J. Kim et al., J. Chem. Phys. **106**, 10207 (1997).

[16] M. Gutowski and P. Skurski, J. Chem. Phys. **107**, 2969 (1997).

[17] M. Gutowski, K. D. Jordan, P. Skurski, J. Phys. Chem. A **102**, 2624 (1998).

[18] C. Leforestier, L. B. Braly, K. Liu, M. J. Elrod, R. J. Saykally, J. Chem. Phys. **106**, 8527 (1997).

[19] B. J. Howard, T. R. Dyke, W. Klemperer, J. Chem. Phys. **81**, 5417 (1984).

[20] H. S. Gutowsky, C. Chuang, J. D. Keen, T. D. Klots, T. Emilsson, J. Chem. Phys. **83**, 2070 (1985).

[21] W. J. Lafferty, R. D. Suenram, F. J. Lovas, J. Mol. Spectrosc. **123**, 434 (1987).

[22] D. H. Zhang, Q. Wu, Z. H. Zhang, M. von Dirke, Z. Bacic, J. Chem. Phys. **102**, 2315 (1995).

[23] M. D. Marshall, P. Jensen, P. R. Bunker, Chem. Phys. Lett. **176**, 255 (1991).

[24] P. R. Bunker, P. Jensen, A. Karpfen, M. Kofranek, H. Lischka, J. Chem. Phys. **92**, 7432 (1990).

[25] S. C. Althorpe, D. C. Clary, P. R. Bunker, Chem. Phys. Lett. **187**, 345 (1991).

[26] H. Sun and R. O. Watts, J. Chem. Phys. **92**, 603 (1990).

[27] H. Sun and R. O. Watts, J. Chem. Phys. **95**, 28 (1991).

[28] W. Klopper, M. Quack, M. A. Suhm, Chem. Phys. Lett. **261**, 35 (1996).

[29] J. A. Pople et al., Gaussian98 (Gaussian, Inc., Pittsburgh, PA, 1998).

TABLE I

Energies (in meV, with respect to dissociated monomers) of the two lowest vibrational states (v=0 and 1) in the tunneling mode of the anionic and neutral hydrogen fluoride dimers split into pairs by tunneling. Note the dramatic reduction of the tunneling splitting in $(HF)_2^-$, which is a measurable fingerprint of double tunneling.

	$(HF)_2^-$	$(HF)_2$
$v=0^+$	-231.0676	-186.9799
$v=0^-$	-231.0671	-186.8882
$v=1^+$	-206.4364	-167.1485
$v=1^-$	-206.4191	-165.1572

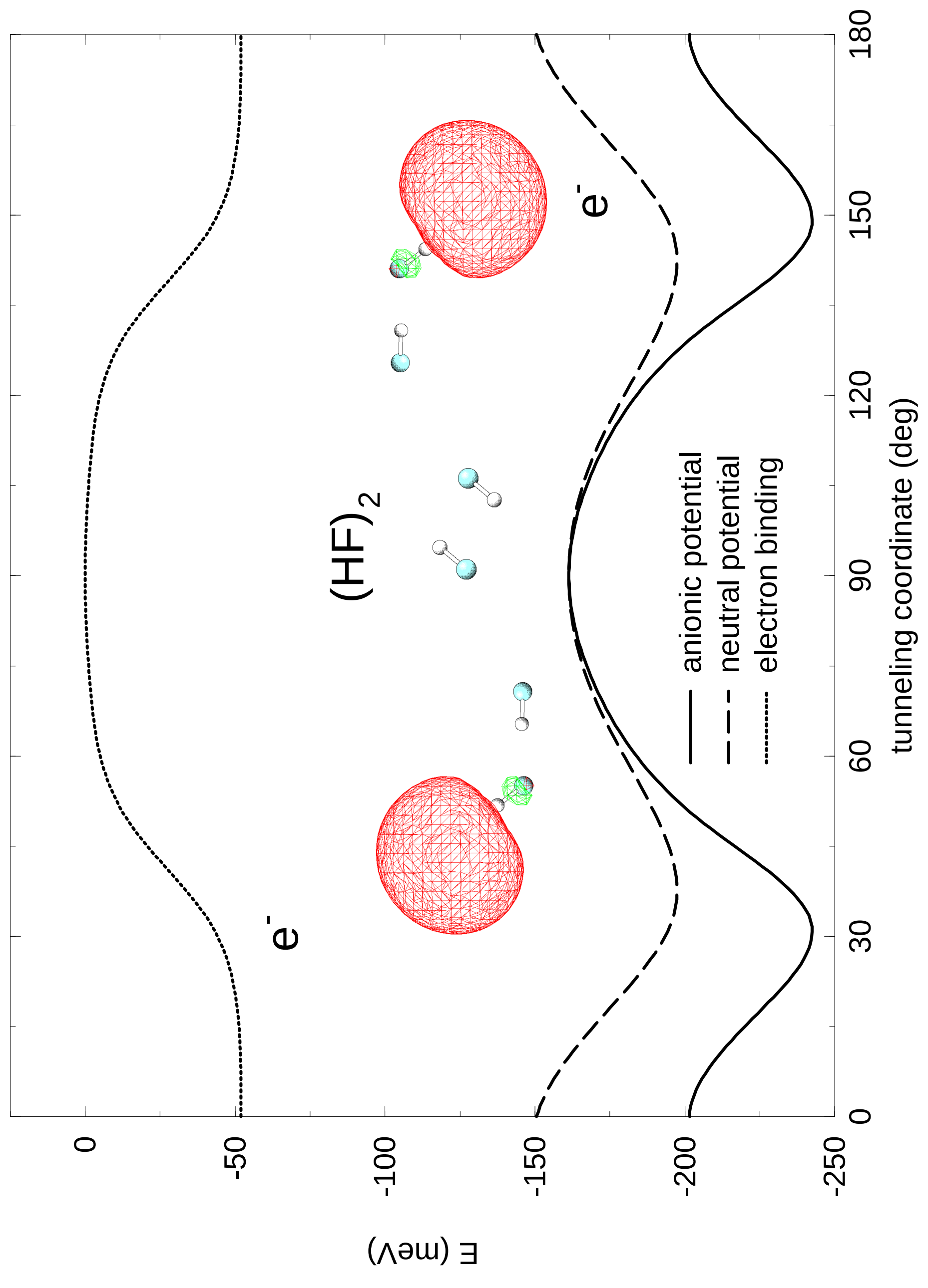

FIG. 1. Double well potentials (energies relative to dissociated monomers), electron binding and molecular structures along the tunneling coordinate. Note the geometries of the hydrogen fuoride dimer (H - smaller balls and F - larger balls in the ball and stick molecular model) and the wavefunction of the excess electron indicating the double tunneling process.

Fig. 2

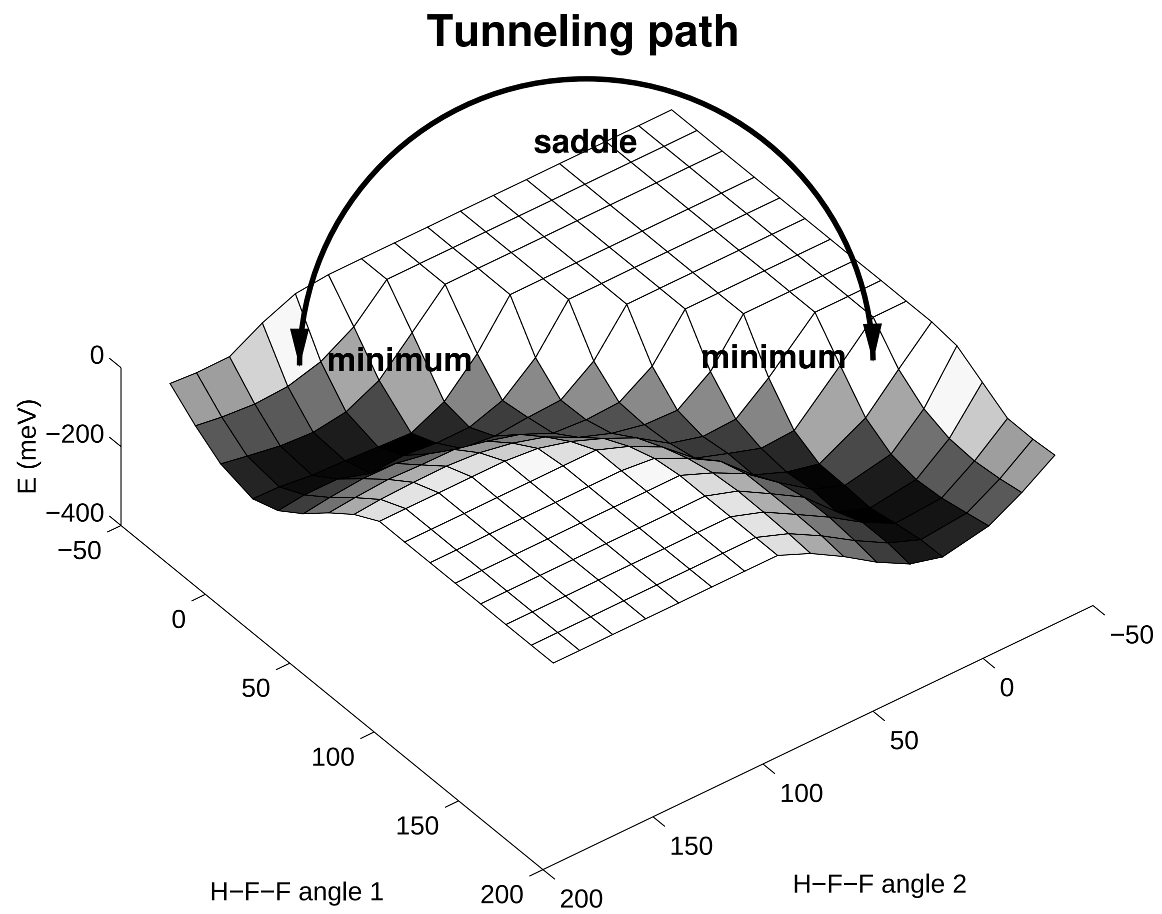

FIG. 2. Two-dimensional representation of the $(HF)_2^-$ potential energy surface as a function of the two H-F-F angles (r_{HF} = 0.928 Å, r_{FF} = 2.723 Å, and the dimer is kept planar). The tunneling path with two equivalent minima separated by a saddle is roughly a part of a circle on this graph. For a better graphical representation the surface is cut at the dissociation energy.