

Comment

Comment on: ‘A symmetric hydrogen bond revisited: potassium hydrogen maleate by variable temperature, variable pressure neutron diffraction and plane-wave DFT methods’ [Chem. Phys. Lett. 381 (2003) 102]

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Abstract

In their recent Letter Wilson, Thomas and Morrison [Chem. Phys. Lett. 381 (2003) 102] questioned the hydrogen bonding potential function in potassium hydrogen maleate that was proposed by Fillaux, Leygue, Tomkinson, Cousson and Paulus [Chem. Phys. 244 (1999) 387]. Wilson et al.’s argument is not supported by any new experimental data of significance. Moreover, the plane-wave DFT potential they calculate for the hydrogen bond was determined in a range of little significance to the experimental data. Fillaux et al.’s potential still represents the fullest description of the totality of experimental observations.

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Potassium hydrogen maleate (KHM) is a prototypical example of a strong symmetric intramolecular hydrogen bond. Fillaux et al. [1] proposed a potential function to account for the proton’s dynamics along the hydrogen bond. The unusual shape of the potential was dictated by the large number (seven) of ν OH bands observed between 500 and 1300 cm^{-1} with the inelastic neutron scattering (INS) technique. These bands were unambiguously assigned thanks to measurements on oriented single crystals of fully hydrogenated and partially deuterated derivatives. Moreover, the extent of the proton’s ground state wave function compared favourably with the temperature factor of 0.016 Å^2 determined from single-crystal neutron diffraction data.

The unusual potential has a sharp, deep, well at the centre of the hydrogen bond and two secondary minima

at $\approx 1000 \text{ cm}^{-1}$ above the central minimum. These secondary minima are located at $\approx \pm 0.8 \text{ Å}$, away from the centre. They show that the hydrogen bond geometry is no longer stable upon excitation of ν OH modes above 500 cm^{-1} . It was concluded that whilst the ground state wave function is ‘hydrogen-bonding’ the excited vibrational states are ‘hydrogen-nonbonding’. The potential shape is a snapshot of the dissociation of the hydrogen bond upon excitation of the OH stretching mode. The apparent paradox of a modest dissociation energy threshold observed in one of the ‘strongest’ known hydrogen bonds was ascribed to partial compensation of the energy of formation of the hydrogen bond by a strain energy arising from the planarity of the maleate ring.

In a recent Letter, Wilson et al. [2] questioned this potential as follows: ‘... the derived potentials [of Fillaux et al.] are by no means of a general nature and the physical basis of these is not obvious.’ We agree with the first part of that statement, since the potentials were

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specifically designed for the KHM crystal. The second part is wrong. The physical basis of the potential is the extensive quantitative agreement between the model potential proposed and the diffraction and vibration data measured.

Wilson et al.'s suggestion that ... 'Such empirical fits can be used to explain the INS data but do not yield wider interpretations of, for example, the diffraction data we are considering here' ... is clearly a fallacy since the Fillaux et al. potential is consistent with the single-crystal neutron diffraction data measured at 5, 14 and 300 K [1]. Wilson et al. provide no new crystallographic data for structures reported at 20 and 300 K (at ambient pressure), they are identical to those given by Fillaux et al. Wilson et al. do, however, nicely confirm that there is virtually no temperature effect on the hydrogen bond, as already emphasized in [1]. In addition, Wilson et al. conclude that there is no observable pressure effect (below 4 kbars). None of Wilson et al.'s data contradicts Fillaux et al.'s proposed potential.

Wilson et al. also calculated a potential curve for the hydrogen bond using the plane-wave (PW) DFT method (see Fig. 4 of [2]). They concluded: ... 'as is widely accepted, the potential energy surface for a strong hydrogen bond in the solid state is indeed a single flattened potential well.' We show below that Wilson et al.'s calculations were carried out over too short a range of proton displacements with respect to the equilibrium position. It is impossible to obtain any relevant information from their calculation for comparison with vibrational spectra or diffraction data.

A cursory comparison of Wilson et al.'s potential (grey line in Fig. 1) with the Fillaux et al. potential (dash line in Fig. 1) may suggest that the two potentials are different in the narrow range of proton positions spanned by the PW-DFT calculations. However, this conclusion is misleading because the calculations were performed in a range where the potential energy is well below the zero-point energy.

In order to compare the two potentials their eigenstates and wavefunctions must be compared. (Recalling that within the framework of quantum mechanics only eigenstates and squared wave functions are observables and potential functions are operators.) We have digitised the Wilson et al. potential, from [2], and determined a best fitting polynomial function (see dot dash line Fig. 1). The coincidence of the ground states for the two potentials gives virtually identical probability densities for the proton. The fitting with a polynomial function is certainly not unique, but this does not alter the conclusion that the two potentials cannot be distinguished from diffraction data. Indeed, the Wilson et al. potential by no means offers ... 'wider interpretations of diffraction data'.

It is worth mentioning that the rather flat PW-DFT potential cannot be fitted with a Gaussian well analo-

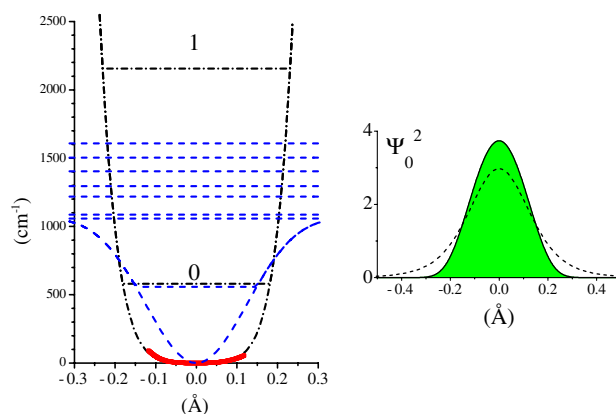


Fig. 1. Extrapolated potential function V , energy levels (dot dash lines, left-hand side) and squared wavefunction (right-hand side, filled) for the best fit to the potential calculated by Wilson et al. in [2] (grey solid line). $V = 1852x^2 + 97616x^4 + 11796 \times 10^3 x^6$ with V and x in cm^{-1} and \AA units, respectively. The abscissa is relative to the hydrogen bond centre. The potential function previously determined by Fillaux et al. [1], the corresponding vibrational states and the squared wavefunction are superimposed (dash lines) for the sake of comparison.

gous to that used by Fillaux et al., as the latter is very close to a parabola around the minimum (see Fig. 1).

Moreover, in contrast to the Fillaux et al. potential, extrapolation of the Wilson et al. potential is quite unable to account for the proton dynamics. Their potential predicts ν OH frequencies far beyond the many transitions observed between 500 and 1300 cm^{-1} in the infrared and INS [1]. The PW-DFT calculations must be extended to a much broader domain of proton positions in order to be reasonably compared with experimental data. En passant, the discussion developed by Wilson et al. aimed at distinguishing between single and double minimum potentials is pointless since the potential barrier under consideration, as shown in Fig. 4 of [2], is negligible compared to the zero-point energy.

In conclusion, Wilson et al. produce no new experimental facts or numerical calculations that contradict the Fillaux et al. potential. They have calculated a part of the potential function that is irrelevant for the determination of the probability density in the ground state. They deliberately ignore the quantum nature of protons and the significant role that can be played by vibrational spectra. They also speculate dubiously about double well potentials in the quantum regime where the barriers are quite below the ground state.

The Fillaux et al. potential for the hydrogen bond in KHM, based on an unprecedented number of firmly assigned energy levels and exhaustive single-crystal neutron diffraction measurements still offers the best view of proton dynamics ever determined exclusively from experimental data. Alternative potential functions accounting for all of these observations may be possible but, owing to the large number of observables, it can be claimed that suitable potentials should be similar in

shape to those already published, irrespective of the choice of any particular analytical function. These potentials are, physically, especially well founded. Whether the hydrogen bond in KHM is unique or if similar potentials also apply to other strong symmetric hydrogen bonds remains an open question.

References

- [1] F. Fillaux, N. Leygue, J. Tomkinson, A. Cousson, W. Paulus, *Chem. Phys.* 244 (1999) 387.
- [2] C.C. Wilson, L.H. Thomas, C.A. Morrison, *Chem. Phys. Lett.* 381 (2003) 102.