SUPPLEMENTARY MATERIAL

Electronic quantum fluxes in vibrating symmetric and polar single, double and triple bonds

Matthias Berg^a, Beate Paulus^{a*} and Timm Bredtmann^b

^a*Institute for Chemistry und Biochemistry,
Free University Berlin, Takustr. 3, 14195 Berlin, Germany;*

^b*Max Born Institute, Max-Born-Strasse 2A, 12489 Berlin, Germany*

* Corresponding author. Email: b.paulus@fu-berlin.de

H_nXYH_n	$R_{XY, \min}$ ($\text{\AA}$)	$\overset{\rho_{\text{el}}}{R_{XY, \max}}$ ($\text{\AA}$)	$\overset{\rho_{\text{nuc}}}{\zeta_{\min}}$ ($\text{\AA}$)	$\zeta_{\max}$ ($\text{\AA}$)
HCCH	0.8	2.0	0.9	3.0
H ₂ CCH ₂	1.0	2.5	0.5	5.0
H ₃ CCH ₃	1.0	3.0	1.0	3.0
HSiCH	1.3	2.5	1.2	3.0
H ₂ SiCH ₂	1.3	3.0	1.2	3.0
H ₃ SiCH ₃	1.5	3.5	1.3	3.5
HSiSiH	1.5	3.0	1.3	3.0
H ₂ SiSiH ₂	1.5	3.5	1.3	3.0
H ₃ SiSiH ₃	1.5	4.0	1.3	3.5

Table 1. Extension of the grids for the electronic and nuclear densities. Individual time-independent electronic densities were calculated at 64 equally spaced points and nuclear densities were calculated on equally spaced grids of 512 points within the tabulated ranges.

1. Computational Details

Table 1 provides ranges of the regular grids used for the electronic ρ_{el} nuclear ρ_{nuc} densities.

2. Nuclear dynamics

The potential energy curves, Figure 1, within each group of molecules, i.e. one group is ethane, ethene and ethine, show force constants increasing with bond order. Bonds of the same order show force constants decreasing with increasing reduced mass. Thus, the periods of the vibrations increase upon exchanging C by Si and by lowering the bond order. Figure 1 shows snapshots of the corresponding nuclear wave packets at $t = 0$ fs and when the inner turning points are reached at $t = t_{\text{tp}}$ for the first time. To compare the electronic rearrangement in the different bonds, we select the initial nuclear states such, that the amplitude $A = \langle \zeta \rangle(0) - \langle \zeta \rangle(t_{\text{tp}})$ reached within the first vibrational period equals 0.5 $\text{\AA}$ for each system. A comparison of such an equal amplitude scenario to an equal energy scenario for the H_nCCH_n molecules was made in Ref. [1]. The key figures, such as excitation energies with respect to the nuclear ground states, mean bond lengths and vibrational periods of the nuclear quantum dynamics are given in Table 2.

References

- [1] T. Bredtmann, E. Hupf and B. Paulus, Phys. Chem. Chem. Phys. **14**, 15494 (2012).

Figure 1. Potential energy curves from MRCI/cc-pVTZ calculations for the a) organosilicon b) hydrocarbon and c) hydrosilicon model vibrations. Overlaid are two snapshots of nuclear wave packets for each molecule. The wave packets denoted by full lines represent the initial nuclear density while ones denoted by dashed lines show the nuclear density at $t = t_{\text{tp}}$ when the inner turning point is reached for the first time. The heights of the baselines of the wave packet pairs represent the mean total energy $\bar{E}$ of the respective vibration. All wave packets are scaled equally.

Molecule	n	$\langle R_{XY,0} \rangle$, (exp.)	$\langle R_{XY} \rangle$ (0 fs)	$\langle R_{XY} \rangle$ (t_{tp})	T_{vib}	$\bar{E}$
H_nSiCH_n						
Methylsilane	3	1.89, (1.87)	2.19	1.69	50.6	0.59
Silene	2	1.72, (1.70)	2.03	1.53	37.6	1.00
Silyne (linear)	1	1.61	1.91	1.41	29.8	1.49
H_nCCH_n						
Ethane	3	1.53, (1.53)	1.84	1.34	36.0	0.89
Ethene	2	1.34, (1.34)	1.66	1.16	24.8	1.73
Ethine	1	1.21, (1.19)	1.53	1.03	18.4	2.92
H_nSiSiH_n						
Disilane	3	2.36, (2.37)	2.65	2.15	81.2	0.34
Disilene (planar)	2	2.16	2.45	1.95	61.2	0.58
Disilyne (linear)	1	2.00	2.30	1.79	49.6	1.39

Table 2. Nuclear dynamics values: calculated mean equilibrium XY bond length $\langle R_{XY,0} \rangle$ and experimental result in brackets given in Å, mean XY bond length $\langle R_{XY} \rangle(0 \text{ fs})$ at $t = 0 \text{ fs}$ in Å, mean XY bond length at the inner turning point $\langle R_{XY} \rangle(t_{tp})$ in Å, duration of the first vibrational period T_{vib} in fs and the mean total energy $\bar{E}$ of vibration in eV.