Supplementary Material (ESI) for PCCP

Electronic supplement for:

Periodic Bond Breaking and Making in the Electronic Ground State on a Sub-Picosecond Timescale: OH Bending Spectroscopy of Malonaldehyde in the Frequency Domain at Low Temperature

by Nils O. B. Lüttschwager, Tobias N. Wassermann, Stéphane Coussan, Martin A. Suhm

Table S1: Band positions $\tilde{\nu}/\text{cm}^{-1}$, IR intensities $I/\text{km mol}^{-1}$, and Raman activities $A/\text{Å}^4\,\text{u}^{-1}$ from B3LYP and MP2 calculations with the 6-311+G(d) basis set using the Gaussian03 programm package.[1] σ' was calculated from A and $\tilde{\nu}$ using equation 1. By clicking on the normal mode descriptions in the first column, a dynamic gif file of the corresponding normal mode is opened.

	MP2/6-311+G(d)				B3LYP/6-311+G(d)			
	$\tilde{\nu}$	I	A	σ'	$\tilde{\nu}$	I	A	σ'
$\delta C_a H$	1299	180	3.7	17	1291	179	2.2	10
δOH	1409	44	29.4	121	1395	90	17	71
$\delta C_c H$	1428	40	25.3	102	1409	29	7.9	32

For the comparison of theoretical predictions with experimental spectra, a conversion of the Raman scattering activities A, that are calculated by Gaussian03,[1] to the scattering cross sections σ' is useful. Equation 1 applies for the case of a photon counting measurement with a CCD detector and simultaneous detection of polarized and unpolarized light ($\perp^s + \|^s$) at 90° detection geometry like it was used in this work. The polarization vector of the incident laser light was oriented perpendicularly to the plane of detection ($\perp^i$). In equation 1, $\tilde{\nu}_k$ and g_k are the vibrational wavenumber and the degeneracy of the corresponding vibration. $\tilde{\nu}_0$ is the wavenumber of the incident laser light (in this work, $\lambda_0 = 532\,\text{nm}$, i.e. $\tilde{\nu}_0 \approx 18797\,\text{cm}^{-1}$), h and k are Planck's and Boltzmann's constants, c is the speed of light and T the temperature. For the comparison with the supersonic jet expansion spectra, $hc\tilde{\nu}_k \gg kT$ was assumed (corresponding to low temperatures in the expansion).

$$\sigma'\left(90^\circ; \perp^s + \|^s, \perp^i\right) = \frac{2\pi^2 h}{45c\tilde{\nu}_k} \cdot \frac{\left(\tilde{\nu}_0 - \tilde{\nu}_k\right)^3 \tilde{\nu}_0}{1 - \exp\left(-\frac{hc\tilde{\nu}_k}{kT}\right)} \cdot g_k A. \tag{1}$$

References

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople. `Gaussian 03, Revision B.04`. Gaussian Inc., Pittsburgh PA, 2003.