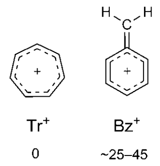
Aromatic Cations

DOI: 10.1002/anie.201008036

On the Benzylium/Tropylium Ion Dichotomy: Electronic Absorption Spectra in Neon Matrices**

*Adam Nagy, Jan Fulara, Iryna Garkusha, and John P. Maier**

$C_7H_7^+$ hydrocarbon cations have been the focus of attention ever since tropylium (Tr^+) was predicted to be highly stable.[1] It fulfills Hückel's rule and is the most common textbook example for aromaticity after benzene. However, the rivalry with its energetically close-lying isomer, benzylium (Bz^+), still poses diverse challenges (Scheme 1). For instance, physical organic chemists have been debating the mass spectrometry data regarding the formation and automerization pathways of these two species generated upon electron impact, photodissociation, ionization/charge transfer, or collisional activation of precursors such as toluene, halotoluenes, benzyl derivatives, or cycloheptatriene.[2,3] Detection schemes are based mainly on the reactivity difference of Bz^+ and Tr^+ in ion–molecule reactions (in particular with toluene), but results are often inconsistent depending on the experimental method. Complications arise primarily because of the fact that the energy of these two ions is computed to differ only by 0.2–0.5 eV (Tr^+ being the global minimum);[3–7] furthermore, the activation barrier for unimolecular isomerization is quite low (ca. 3 eV) and assumed to involve a large variety of transition states.[3–5]



Scheme 1. The two most stable structural isomers of $C_7H_7^+$ with their relative energies (kJ mol^{-1}), taken from Refs. [3–7].

Straightforward structural information can be obtained by spectroscopic means, and even though such studies on $C_7H_7^+$ stem back sixty years, it is a far less explored alternative to the mass spectrometric investigations. The first reported spectrum of Tr^+ revealed a broad ultraviolet (UV) absorption in a low-pH water solution of its bromide salt.[8] The following decades produced a sparse number of additional experimental results on the excited states of the cations in question, including photoelectron spectroscopy for Tr^+,[9] whereas direct absorption in acidic solutions,[10] pulse radiolysis,[11,12] and laser flash photolysis[13] in liquids, as well as a photoionization study in an argon matrix[14] were used to determine the electronic transitions of Bz^+. Despite these efforts, the spectroscopic data for $C_7H_7^+$ is ambiguous. In this contribution, electronic absorption spectra of Bz^+ and Tr^+ recorded after mass-selective trapping of the cations in 6 K neon matrices are presented for the first time.

Figure 1 a shows the absorption spectrum obtained after deposition of mass-selected $C_7H_7^+$ ions produced from cycloheptatriene as precursor into a neon matrix. It is dominated by an extended series of broad bands between approximately 400–520 nm. Several sharp peaks are superimposed onto them commencing at around 450 nm. The use of toluene, benzyl chloride (BzCl), or 1,6-heptadiyne as starting material resulted in essentially the same spectra. The broad features lose and the sharp ones gain intensity upon broadband UV irradiation of the matrix, whereas no additional bands appear (Figure 1 b). UV photons induce electron recombination in

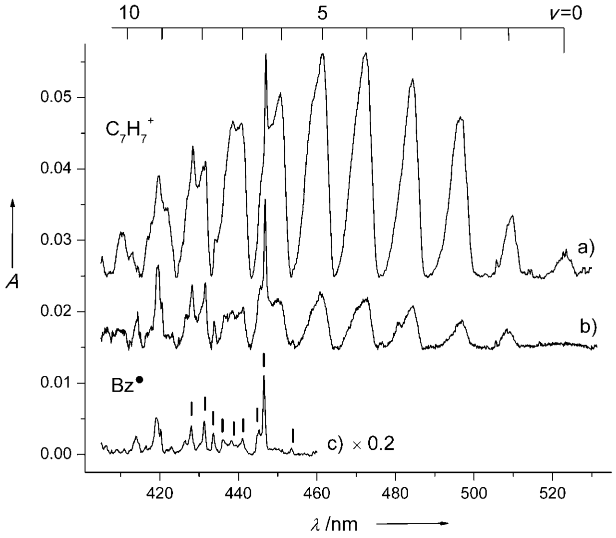


Figure 1. Electronic spectrum observed in the visible spectral region after: a) deposition of mass-selected $C_7H_7^+$ ions produced from cycloheptatriene into a 6 K neon matrix (vibrational progression in the ν_{13} fundamental of Bz^+ is given above) and b) subsequent UV irradiation of the matrix. Deposition of the cations without the use of an electron scavenger (trace c) results in rapid charge neutralization and the formation of benzyl radical. Note that the ionic bands in the latter case are absent and the spectrum is downscaled for comparison.

---

[*] A. Nagy, Dr. hab. J. Fulara,[+] I. Garkusha, Prof. J. P. Maier
Departement Chemie, Universität Basel
Klingelbergstrasse 80, 4056 Basel (Switzerland)
Fax: (+41) 61-267-3855
E-mail: j.p.maier@unibas.ch
Homepage: http://www.chemie.unibas.ch/~maier/

[+] Permanent address: Instytut Fizyki, Polskiej Akademii Nauk
Al. Lotników 32/46, 02668 Warszawa (Poland)

[**] This work has been supported by the Swiss National Science Foundation (project no. 200020-124349/1).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201008036.

the matrix; hence, the decreasing bands are due to cations, while the ones growing belong to neutral species.

The system of narrow bands having the most intense peak at 447 nm is recognized as the visible spectrum of the benzyl neutral radical (Bz$^\bullet$); this data was reported from low-temperature matrices[15] and in the gas phase.[16,17] Although chloromethane, which works as an electron scavenger, was added to the neon host, the bands of Bz$^\bullet$ are weakly seen in Figure 1 a. They result from partial charge neutralization of the deposited $C_7H_7^+$ cations. Scavengers suppress neutralization by capturing free electrons and equilibrating the space charge that develops from cation accumulation during matrix growth.[18] In experiments carried out without CH_3Cl (Figure 1 c), the bands of Bz$^\bullet$ are more intense than in spectra recorded with the scavenger; the absence of the broad, structured absorptions of Figure 1 a is a further indication of the cationic nature of their carrier.

For these reasons and because a mass-selective method was used for cation trapping, the new electronic absorption system shown in Figure 1 a with origin band at 523 nm belongs to $C_7H_7^+$. Furthermore, depositing the ions with the smallest kinetic energy possible quenched the $C_7H_7^+$ fragmentation at the surface—neither $C_5H_5^+$, the easiest accessible channel as shown by dissociation techniques,[19,20] nor a number of other small fragment species that were studied in this laboratory,[21] appeared in any of the experiments.

The visible system of $C_7H_7^+$ has a regular, bell-like Franck–Condon profile (Figure 1 a). It is formed by a number of bands separated from each other by approximately 510 cm^{-1}. Its maximum lies around 460–470 nm and corresponds to 4 or 5 quanta excitation of the mode above in the upper electronic state. The intensity of the system normalized to the same deposited charge of $C_7H_7^+$ does not depend on the precursor used for the production of the cations; therefore, the structure of the $C_7H_7^+$ species cannot be deduced from the topology of the precursor molecules.

Apart from the visible systems shown in Figure 1 a, several absorptions have been detected in the UV range (Figure 2 a). The bands marked with arrows and asterisks decreased in intensity upon UV irradiation of the matrix and thus have cationic origin; the remaining features stem from neutral species because they grew in intensity under the same conditions (Figure 2 b). The neutral absorptions with onsets around 305 and 248 nm are identical with the reported UV spectrum of Bz$^\bullet$;[15,22,23] they arise from the $\tilde{C}^2A_2 \leftarrow \tilde{X}^2B_2$ and $\tilde{D}^2B_2 \leftarrow \tilde{X}^2B_2$ transitions. In the present study, as a result of the high intensity of the $\tilde{C}^2A_2 \leftarrow \tilde{X}^2B_2$ system of Bz$^\bullet$, it was possible to detect several weak vibrational bands not reported in earlier studies. Positions of the band maxima and their assignment are collected in Table S1 (see the Supporting Information). The strong absorptions of Bz$^\bullet$ obscure bands of the cations. To better visualize the features originating from $C_7H_7^+$, absorptions of the radical species (Figure 2 b) have been subtracted, after proper scaling, from the spectrum shown in Figure 2 a. The resulting trace is Figure 2 c.

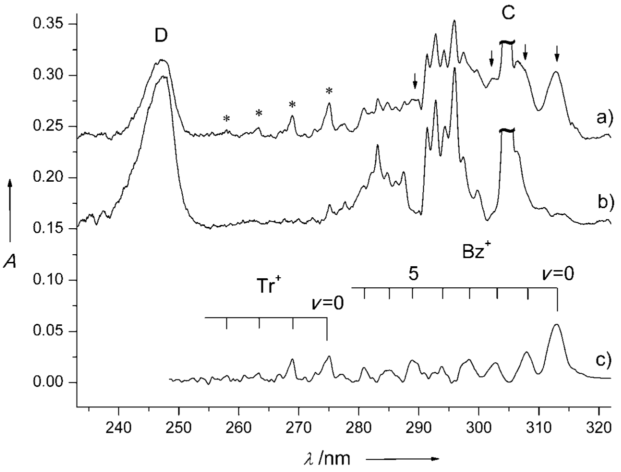


Figure 2. Electronic spectra in the UV observed after: a) deposition of $C_7H_7^+$ and b) photobleaching the matrix. Bands labeled C and D belong to Bz$^\bullet$, whereas asterisks and arrows mark cationic absorptions. In c) trace b) was subtracted from trace a) after scaling it by an appropriate factor to match intensity of band C.

Two band systems of $C_7H_7^+$ can be discerned in Figure 2 c. The first comprises broad, regularly spaced (ca. 510 cm^{-1}) absorptions starting at 313 nm. The second one with onset at 275 nm is formed by narrower bands separated by approximately 840 cm^{-1}. The relative intensity of these two systems varies with the precursors used for the production of $C_7H_7^+$ cations; however, the absorptions in the visible with onset around 523 nm and the UV system at 313 nm maintain the same ratio using different precursors, thus indicating a common origin. The absorptions starting at 275 nm were almost absent in the case of BzCl, while the visible system and that in the UV at 313 nm were quite strong. Therefore, it can be concluded that the former and the two latter systems originate from two isomers of $C_7H_7^+$. Moreover, the fact that only one isomer was produced from BzCl indicates that this is Bz$^+$, because using benzyl chloride for the generation of $C_7H_7^+$ ensures the mildest discharge conditions in the ion source. It is expected that the C−Cl bond dissociates readily, leading to Bz$^\bullet$, which then forms Bz$^+$ upon ionization. In conclusion, the bands with onsets near 523 and 313 nm belong to Bz$^+$.

To support this interpretation, the ground-state energy and vibrational frequencies of the two lowest-lying isomers of $C_7H_7^+$, Tr$^+$ and Bz$^+$, have been calculated with DFT at the BLYP/6-311G(d,p) level of theory using the Gaussian 03 program suite.[24] Results are included as a footnote in Table 1. They confirm earlier studies that Tr$^+$ is the most stable form of $C_7H_7^+$; Bz$^+$ lies 42 kJ mol^{-1} above the global minimum. Although thermal equilibrium in the source during the production of the ions may not be reached, tolylium cations ($CH_3C_6H_4^+$) and adventitious open-chain or bicyclic structures are excluded from consideration on the basis of their significantly higher energy than those of Tr$^+$ and Bz$^+$.[5,6]

The lowest-frequency, totally symmetric vibrational fundamental of Bz$^+$ (in C_{2v}) is ν_{13} at 523 cm^{-1}, which is in agreement with the mode of about 510 cm^{-1} observed in both the visible and UV spectra of Bz$^+$. Tr$^+$ (D_{7h} symmetry) has only two totally symmetric fundamentals, $\nu_1 = 3113$ and $\nu_2 = 847$ cm^{-1}. The absorption system with origin at 275 nm of $C_7H_7^+$ shows a simple progression of energy of approximately 840 cm^{-1}. Therefore, this system is likely to correspond to Tr$^+$.

Table 1: Observed band maxima ($\lambda_{Ne} \pm 0.1$ nm) of electronic transitions of $C_7H_7^+$ cations and their assignments. Results are compared with computed vertical excitation energies ΔE and transition oscillator strengths f (*italic*) from the ground to the lowest excited states.

λ_{Ne} [nm]	ΔE[a] [eV] (f)	$\tilde{\nu}$ [cm^{-1}]	$\Delta\tilde{\nu}$ [cm^{-1}]	Assignment[b]
Bz^+				
523.2	2.73 (*0.0193*)	19113	0	0^0_0 $(1)^1B_1\leftarrow\tilde{X}^1A_1$
509.6		19623	510	ν_{13} (ring distortion)
496.3		20149	1036	$2\nu_{13}$
484.1		20657	1544	$3\nu_{13}$
472.3		21173	2060	$4\nu_{13}$
461.4		21673	2560	$5\nu_{13}$
450.7		22188	3075	$6\nu_{13}$
440.6		22696	3583	$7\nu_{13}$
430.5		23229	4116	$8\nu_{13}$
421.1		23747	4634	$9\nu_{13}$
410.2		24378	5265	$10\nu_{13}$
312.9	4.42 (*0.2257*)	31959	0	0^0_0 $(1)^1A_1\leftarrow\tilde{X}^1A_1$
308.0		32468	509	ν_{13}
303.0		33003	1044	$2\nu_{13}$
298.4		33512	1553	$3\nu_{13}$
293.8		34037	2078	$4\nu_{13}$
288.9		34614	2607	$5\nu_{13}$
285.1		35075	3116	$6\nu_{13}$
280.8		35613	3654	$7\nu_{13}$
Tr^+				
275.1	5.51 (*0.0024*)	36350	0	0^0_0 $^1A''_2\leftarrow\tilde{X}^1A'_1$
268.9		37189	839	ν_2 (ring breathing)
263.3		37979	1629	$2\nu_2$
258.0		38760	2410	$3\nu_2$

[a] Transition energies were obtained from TD DFT calculations at the BLYP/6-311G(d,p) level of theory. For Tr^+, excited states were assumed to keep the D_{7h} molecular symmetry; however, they may be affected by Jahn–Teller distortion and split into C_{2v} resonance structures (see Ref. [25] for the case of the tropyl neutral radical). [b] Vibrational assignment in the excited states is based on totally symmetric modes (cm^{-1}) in the ground state of Bz^+ (a_1 in C_{2v}): 3137, 3119, 3112, 3070, 1605, 1538, 1456, 1346, 1183, 990, 975, 798, 523; and of Tr^+ (a'_1 in D_{7h}): 3113, 847—obtained with DFT at the BLYP/6-311G(d,p) level of theory. Energies (E_h, not corrected for ZPE) are as follows: −270.60338 (Bz^+) and −270.61928 (Tr^+).

More relevant to the present experimental studies are the excitation energies of Bz^+ and Tr^+. They were calculated using a time-dependent (TD) DFT method with the BLYP functional and the 6-311G(d,p) basis set. Results of these calculations are collected in Table 1. For Bz^+, a moderately intense electronic transition is predicted in the visible region around 453 nm (oscillator strength $f \approx 0.02$), which is within the expected vicinity of the origin band at 523 nm using the TD DFT method. Two other transitions are located in the UV range: the strongest ($f \approx 0.2$) near 281 nm and a very weak one ($f \approx 0.0002$) around 277 nm. The calculated excitation energy of the UV transition of Bz^+ at 281 nm matches well the origin observed at 313 nm. The integrated intensity of the band system with onset at 523 nm is about five times less than that of the one in the UV region with origin at 313 nm; the calculations give an intensity ratio of the visible to the UV transition of 12. Based on these theoretical results, the absorptions with onsets at 523 and 313 nm are assigned to the $(1)^1B_1\leftarrow\tilde{X}^1A_1$ and $(1)^1A_1\leftarrow\tilde{X}^1A_1$ transitions of Bz^+.

TD DFT computations carried out on Tr^+ (Table 1) revealed two allowed electronic transitions from the $\tilde{X}^1A'_1$ ground state: a weaker one ($f \approx 0.002$) around 225 nm to the $^1A''_2$ state, and a much stronger ($f \approx 0.6$) around 202 nm to the $^1E'_1$ state. If the absorptions with onset at 275 nm originate from Tr^+, then the calculations overestimate its excitation energy by about 1 eV. This discrepancy can partially result from the fact that calculations give the vertical excitation energy; the other reason could be the multireference character of the $^1A''_2$ state. The predicted $^1E'_1\leftarrow\tilde{X}^1A'_1$ transition around 202 nm could not be detected in the present study because of strong light scattering precluding measurements there.

A photoelectron study on the tropyl radical, generated by the pyrolysis of bitropyl, revealed that the first excited state of Tr^+ is $^3E'_3$, lying 3.4 eV higher than the ground state.[9] Upon examination of the reported spectrum, there is another band spaced about 4.4 eV (ca. 284 nm) above the ground state of the cation and it agrees well with the origin of the second isomer of $C_7H_7^+$ observed at 275 nm. Hence, results of that study validate our quantum chemical calculations and lead to the conclusion that the absorptions with onset at 275 nm originate from Tr^+. Furthermore, the reported UV spectrum of Tr^+ in strong acidic solutions has a maximum at 275 nm.[8,20]

UV electronic transitions of Bz^+ have been studied in the past using different methods: low-pH solutions,[10] pulse radiolysis,[11,12] laser flash photolysis,[13] and photoionization in an argon matrix.[14] The spectra obtained did not agree with each other. The most plausible results were obtained in a pulse radiolysis experiment on liquid BzCl containing O_2, ethanol, or pyrrole as radical or ion interceptors; they quenched the transient absorptions to a different extent.[11] Two broad, structureless absorptions of Bz^+ with maxima at 304 (strongest) and 500 nm have been reported. The spectrum agrees well with the present neon matrix data; however, neon is a less perturbing environment and reveals well-resolved vibrational structure.

In summary, the two most stable $C_7H_7^+$ isomers, benzylium and tropylium, have been trapped and identified in neon matrices. Hitherto, electronic spectroscopy of these species was not fully understood. The present study on the mass-selected cations reveal a weak $(1)^1B_1\leftarrow\tilde{X}^1A_1$ and a much stronger $(1)^1A_1\leftarrow\tilde{X}^1A_1$ transition for Bz^+ (C_{2v}), and the lowest dipole-allowed $^1A''_2\leftarrow\tilde{X}^1A'_1$ absorption for Tr^+ (D_{7h}). These findings provide reliable starting data for gas-phase investigations.

Experimental Section

Electronic spectra were recorded after deposition of mass-selected cations into neon matrices. The apparatus has been described.[26] Ions were produced in a hot-cathode discharge source from 15–30% mixture or precursor vapors (cycloheptatriene, toluene, benzyl chloride, or 1,6-heptadiyne) with helium. After extraction from the source, the beam was deflected by 90° and directed, using electrostatic lenses, into a quadrupole mass filter, where $C_7H_7^+$ ions ($m/z = 91$) were selected with a ±0.5 u resolution. They were then co-deposited over a period of 2–6 h with excess of neon onto a rhodium-coated sapphire plate held at 6 K. CH$_3$Cl diluted in the neon host in a ratio 1:20000 was used as an electron scavenger.

After growing the matrix to approximately 150 μm thickness and accumulating a total nominal charge 100–500 μC under the best experimental conditions, the cations reached a density of about 10^{16} cm^{-3}. Absorption spectra of the trapped species were recorded in the 220–1100 nm range by probing the matrix parallel to the substrate surface (2 cm long) in a "waveguide" manner, using halogen/xenon light sources, a monochromator, and photomultiplier/silicon diode detectors. Irradiation of the matrix with UV photons from a medium-pressure mercury arc ("photobleaching") was used to distinguish transitions of positively charged species from those of neutrals.

Received: December 20, 2011

Keywords: benzylium · electronic spectra · matrix isolation · tropylium · UV/Vis spectroscopy

---

[1] a) E. Hückel, *Z. Phys.* **1931**, *70*, 204; b) J. L. Franklin, F. H. Field, *J. Am. Chem. Soc.* **1953**, *75*, 2819.

[2] a) C. Lifshitz, *Acc. Chem. Res.* **1994**, *27*, 138, and references therein; b) E.-L. Zins, C. Pepe, D. Schröder, *Faraday Discuss.* **2010**, *145*, 157; c) M. Malow, M. Penno, K.-M. Weitzel, *J. Phys. Chem. A* **2003**, *107*, 10625; d) M. Schwell, F. Dulieu, C. Gée, H.-W. Jochims, J.-L. Chotin, H. Baumgärtel, S. Leach, *Chem. Phys.* **2000**, *260*, 261; e) S. K. Shin, B. Kim, R. L. Jarek, S.-J. Han, *Bull. Korean Chem. Soc.* **2002**, *23*, 267; f) J. H. Moon, J. C. Choe, M. S. Kim, *J. Phys. Chem. A* **2000**, *104*, 458.

[3] T. D. Fridgen, J. Troe, A. A. Viggiano, A. J. Midey, S. Williams, T. B. McMahon, *J. Phys. Chem. A* **2004**, *108*, 5600.

[4] a) K. W. Bullins, T. T. S. Huang, S. J. Kirkby, *Int. J. Quantum Chem.* **2009**, *109*, 1322; b) B. J. Smith, N. E. Hall, *Chem. Phys. Lett.* **1997**, *279*, 165.

[5] I. S. Ignatyev, T. Sundius, *Chem. Phys. Lett.* **2000**, *326*, 101.

[6] a) S.-J. Kim, C.-H. Shin, S. K. Shin, *Mol. Phys.* **2007**, *105*, 2541; b) C.-H. Shin, K.-C. Park, S.-J. Kim, B. Kim, *Bull. Korean Chem. Soc.* **2002**, *23*, 337; c) S. K. Shin, *Chem. Phys. Lett.* **1997**, *280*, 260.

[7] a) J. C. Choe, *J. Phys. Chem. A* **2008**, *112*, 6190; b) J. C. Choe, *Chem. Phys. Lett.* **2007**, *435*, 39.

[8] W. von E. Doering, L. H. Knox, *J. Am. Chem. Soc.* **1954**, *76*, 3203.

[9] T. Koenig, J. C. Chang, *J. Am. Chem. Soc.* **1978**, *100*, 2240.

[10] a) G. A. Olah, C. U. Pittman, Jr., R. Waack, M. Doran, *J. Am. Chem. Soc.* **1966**, *88*, 1488; b) I. Hanazaki, S. Nagakura, *Tetrahedron* **1965**, *21*, 2441; c) J. A. Grace, M. C. R. Symons, *J. Chem. Soc.* **1959**, 958.

[11] N. Fujisaki, P. Comte, T. Gäumann, *J. Chem. Soc. Chem. Commun.* **1993**, 848.

[12] a) L. M. Dorfman, R. J. Sujdak, B. Bockrath, *Acc. Chem. Res.* **1976**, *9*, 352; b) R. L. Jones, L. M. Dorfman, *J. Am. Chem. Soc.* **1974**, *96*, 5715.

[13] a) F. L. Cozens, V. M. Kanagasabapathy, R. A. McClelland, S. Steenken, *Can. J. Chem.* **1999**, *77*, 2069; b) R. A. McClelland, C. Chan, F. Cozens, A. Modro, S. Steenken, *Angew. Chem.* **1991**, *103*, 1389; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1337.

[14] L. Andrews, B. W. Keelan, *J. Am. Chem. Soc.* **1981**, *103*, 99.

[15] a) L. Andrews, J. H. Miller, B. W. Keelan, *Chem. Phys. Lett.* **1980**, *71*, 207; b) D. M. Friedrich, A. C. Albrecht, *Chem. Phys.* **1974**, *6*, 366; c) G. Porter, E. Strachan, *Spectrochim. Acta* **1958**, *12*, 299.

[16] G. C. Eiden, J. C. Weisshaar, *J. Chem. Phys.* **1996**, *104*, 8896.

[17] K. Tonokura, M. Koshi, *J. Phys. Chem. A* **2003**, *107*, 4457, and references therein.

[18] J. Fulara, A. Nagy, I. Garkusha, J. P. Maier, *J. Chem. Phys.* **2010**, *133*, 024304.

[19] P. Lablanquie, K. Ohashi, N. Nishi, *J. Chem. Phys.* **1993**, *98*, 399, and references therein.

[20] D. A. McCrery, B. S. Freiser, *J. Am. Chem. Soc.* **1978**, *100*, 2902.

[21] Unpublished results include electronic absorption spectra of $C_7H_n^{+/0}$ ($n = 4$–6), $C_5H_n^{+/0}$ ($n = 3$–6) and other cationic/neutral hydrocarbons.

[22] B. Ward, *Spectrochim. Acta Part A* **1968**, *24*, 813.

[23] a) M. Margraf, B. Noller, C. Schröter, T. Schultz, I. Fischer, *J. Chem. Phys.* **2010**, *133*, 074304; b) F. Markert, P. Pagsberg, *Chem. Phys. Lett.* **1993**, *209*, 445; c) N. Ikeda, N. Nakashime, K. Yoshihara, *J. Phys. Chem.* **1984**, *88*, 5803.

[24] Gaussian 03 (Revision C.01): M. J. Frisch et al.; see the Supporting Information.

[25] a) I. Sioutis, V. L. Stakhursky, Gy. Tarczay, T. A. Miller, *J. Chem. Phys.* **2008**, *128*, 084311; b) V. L. Stakhursky, I. Sioutis, Gy. Tarczay, T. A. Miller, *J. Chem. Phys.* **2008**, *128*, 084310.

[26] P. Freivogel, J. Fulara, D. Lessen, D. Forney, J. P. Maier, *Chem. Phys.* **1994**, *189*, 335.