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Carbocations

IR Spectrum of the Ethyl Cation: Evidence for the Nonclassical Structure**

*Horia-Sorin Andrei, Nicola Solcà, and Otto Dopfer**

The ethyl cation ($C_2H_5^+$) is a fundamental carbocation in hydrocarbon chemistry. It results from protonation of ethene, the smallest member of the alkene family. $C_2H_5^+$ is a ubiquitous ion in terrestrial and extraterrestrial hydrocarbon plasmas[1] and mass spectra of many hydrocarbon molecules.[2,3] In addition, $C_2H_5^+$ is a popular protonating agent in chemical-ionization mass spectrometry. From a theoretical viewpoint, $C_2H_5^+$ is a benchmark ion, because its nonclassical and classical structures, **1** and **2** (Figure 1), are predicted to be close in energy. Although a plethora of theoretical and experimental studies are consistent with a nonclassical equilibrium structure, convincing experimental confirmation is still lacking. Herein we report the IR spectrum of $C_2H_5^+$, which provides the first clear experimental evidence that **1** is indeed the most stable structure of this fundamental carbocation.

Numerous quantum chemical calculations demonstrate that structure **1** with C_{2v} symmetry and a three-center two-electron bond is the global minimum on the potential-energy surface (PES) in the $^1A_1$ ground electronic state of $C_2H_5^+$.[4] There are no other minima on the $C_2H_5^+$ PES. In particular, all classical structures collapse into **1** as soon as electron correlation effects are taken into account. One such classical structure with C_s symmetry, namely **2**, is the low-lying transition state for intramolecular proton scrambling by connecting equivalent global minima of **1** with a calculated barrier of 20–35 $kJ\,mol^{-1}$. In contrast to the cation, calculations and spectroscopy show that the C_2H_5 radical has a classical geometry ($CH_3{-}CH_2$), with low barriers to internal CH_3 rotation but high barriers for proton scrambling.[5]

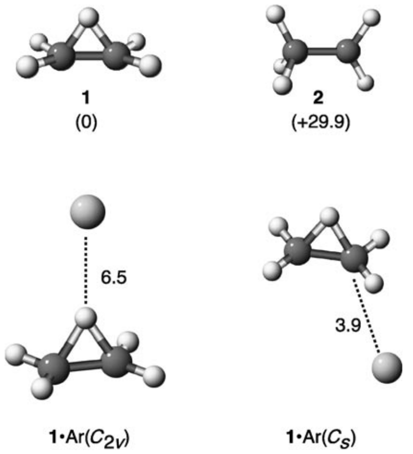

Figure 1. Structures, relative energies [$kJ\,mol^{-1}$] (top), and intermolecular binding energies [$kJ\,mol^{-1}$] (bottom) of isomers of $C_2H_5^+$ and $C_2H_5^+$·Ar calculated at the MP2/6-311G(2df,2pd) level.

Despite considerable efforts, gas-phase experiments have been unsuccessful in determining the structure of isolated $C_2H_5^+$. Early mass spectrometric reactivity experiments on isotopically labeled $C_2H_5^+$ showed evidence for rapid and statistical proton/deuteron scrambling, and thus confirmed the low predicted isomerization barriers.[6] The interpretation of photoionization and photoelectron spectra[4f,7,8] of C_2H_5 suffers from the large change in geometry on ionization. As a result of small Franck–Condon factors near the ionization threshold, experimental values of the adiabatic ionization potentials show large variations ((8.39 ± 0.02) eV,[7a] $\leq(8.26\pm0.02)$ eV,[7b] (8.117 ± 0.008) eV),[4f] and the assignment of the dense and irregular vibrational structure of the nonrigid $C_2H_5^+$ cation remains controversial.[4f,7,8] An alternative direct route to unambiguously determining the structure of isolated $C_2H_5^+$ is provided by IR spectroscopic techniques. However, in contrast to related nonclassical carbocations (CH_5^+,[9] $C_2H_3^+$,[10] $C_2H_7^+$),[11] IR spectra of $C_2H_5^+$ have not been reported.[12]

Although never directly observed as a stable species in solution,[13] $C_2H_5^+$ has been invoked as reactive intermediate in rearrangements of alkyl cations. Analysis of the reaction products of isotopically labeled $C_2H_5^+$ ions in superacid solutions revealed rapid proton scrambling with estimated isomerization barriers of less than 8 $kJ\,mol^{-1}$.[14] These barriers are lower than the value calculated for isolated $C_2H_5^+$, that is, solvation may stabilize **2** with respect to **1**,[15] for example, by interaction of a nucleophilic solvent with the positive charge on the sp^2 carbon center.[4k]

High-pressure mass spectrometric studies on size-selected $C_2H_5^+{\cdot}L_n$ clusters (e.g., L = OCS, CO_2, N_2O, CH_4, N_2, H_2, noble gas)[16] demonstrated mainly formation of weakly bound aggregates without reaction, with binding enthalpies between about 7 (L = Ar) and about 50 $kJ\,mol^{-1}$ (L = N_2O).[17] However, no structural information on the $C_2H_5^+$ ion core could be obtained, although accompanying quantum chemical calculations suggested that the geometry of $C_2H_5^+$ sensitively depends on the type of solvent and the degree of solvation.

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[*] Dipl.-Phys. H.-S. Andrei, Dr. N. Solcà,[+] Prof. Dr. O. Dopfer
Institut für Optik und Atomare Physik
Technische Universität Berlin
Hardenbergstrasse 36, 10623 Berlin (Germany)
Fax: (+49) 30-3142-3018
E-mail: dopfer@physik.tu-berlin.de

[+] Current address:
Laboratorio Cantonale
Via Mirasole 22, 6500 Bellinzona (Switzerland)

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We employed the highly sensitive technique of single-photon IR photodissociation (IRPD) spectroscopy of mass-selected ions[18] to unambiguously determine the geometry of $C_2H_5^+$. As the dissociation energy of $C_2H_5^+$ ($E \approx 200\,\mathrm{kJ\,mol^{-1}}$ for fragmentation into $C_2H_3^+ + H_2$)[3,4j] exceeds typical IR photon energies ($h\nu_{IR} < 50\,\mathrm{kJ\,mol^{-1}}$), an Ar atom was attached to the ions to facilitate resonant single-photon fragmentation [Ar tagging, Eq. (1)].[19]

$$C_2H_5^+ \cdot \mathrm{Ar} + h\nu_{IR} \rightarrow C_2H_5^+ + \mathrm{Ar} \qquad (1)$$

Comparison of the IR spectra calculated for **1** and **2** in Figure 2 reveals that the two isomers can readily be distinguished in the CH stretching region. Significantly, the spectrum of **2** displays intense absorptions near 2750 $\mathrm{cm^{-1}}$ characteristic for CH stretching modes of the CH_3 group (sp^3 hybridization). In contrast, the spectrum of **1** features a distinct absorption near 3000 $\mathrm{cm^{-1}}$ typical of the nonclassical structure. To investigate the effect of Ar on the spectroscopic properties of **1**, the minimum structures and IR spectra of possible **1**·Ar isomers were calculated. Only two minima, namely, **1**·Ar(C_{2v}) and **1**·Ar(C_s), were found (Figure 1), with binding energies of 6.5 and 3.9 $\mathrm{kJ\,mol^{-1}}$, respectively. These values are consistent with the experimental binding enthalpy of approximately 7 $\mathrm{kJ\,mol^{-1}}$ measured for $C_2H_5^+\cdot$Ar.[16e] Significantly, these intermolecular Ar binding energies are well below the energy difference between **1** and **2** (ca. 30 $\mathrm{kJ\,mol^{-1}}$). Consequently, Ar complexation has nearly no effect on the geometry of $C_2H_5^+$ ($\Delta R_{CH} < 0.0002$ Å) and its IR spectrum in the CH stretching range (Figure 2, $\Delta\tilde{\nu}_{CH} < 2\,\mathrm{cm^{-1}}$), and thus Ar-tagging IRPD spectroscopy is a suitable tool to identify the geometry of $C_2H_5^+$.[20,21]

The IRPD spectrum of $C_2H_5^+\cdot$Ar in Figure 2e closely resembles the theoretical spectra of **1** and **1**·Ar but shows large deviations from the spectrum predicted for **2**. Clearly, the $C_2H_5^+$ core of the observed $C_2H_5^+\cdot$Ar species has a nonclassical structure, and this is convincing evidence that **1** is indeed the most stable structure of $C_2H_5^+$. The two detected bands A and B at 3117 and 3037 $\mathrm{cm^{-1}}$ are close to the absorptions predicted for **1**·Ar(C_{2v}) at 3117 and 2996 $\mathrm{cm^{-1}}$, which can be assigned to the asymmetric CH stretching modes of the nearly planar C_2H_4 moiety with b_1 and b_2 symmetry, respectively.[22] Closer inspection of bands A and B reveals a partly resolved rotational substructure (Figure 3). The observed rotational profiles are compatible with simulations of c-type (band A, pronounced Q branch) and b-type (band B, no Q branch) transitions of **1**·Ar(C_{2v}), under the assumption of a rotational temperature of $T = 50$ K, nuclear spin statistical weights appropriate for four equivalent protons, relative IR intensities and ground-state rotational constants taken from the ab initio equilibrium structure, and rotational constants for the vibrational excited state derived for an averaged elongation of 0.005 Å of the C–H bonds on vibrational excitation.[23] The agreement between experimental and simulated band contours provides further confidence in the observation of **1**·Ar(C_{2v}), which is calculated to be the most stable $C_2H_5^+\cdot$Ar isomer.

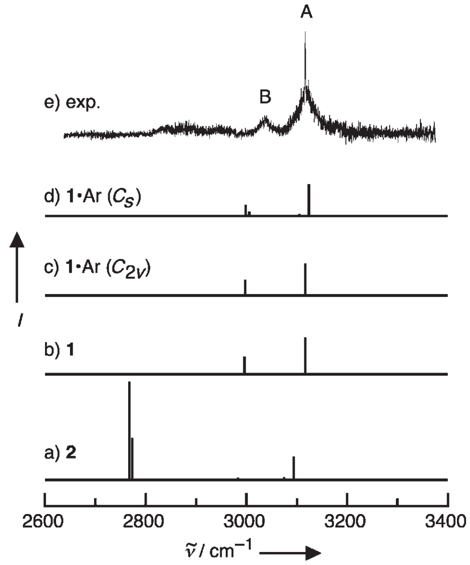

Figure 2. Linear stick IR absorption spectra of a) **2**, b) **1**, c) **1**·Ar(C_{2v}), and d) **1**·Ar(C_s) calculated at the MP2/6-311G(2df,2pd) level (scaling factor of 0.9419) in comparison to the experimental IRPD spectrum of $C_2H_5^+\cdot$Ar (e).

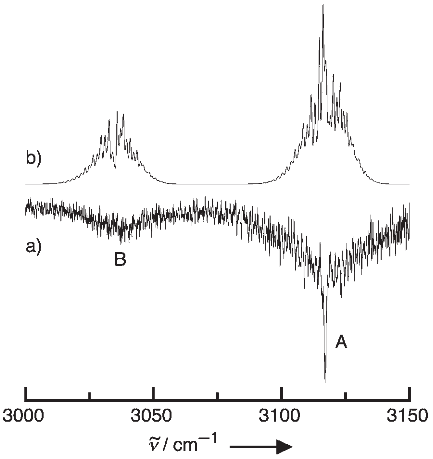

Figure 3. a) Experimental IRPD spectrum of $C_2H_5^+\cdot$Ar. b) Simulated IR spectrum of **1**·Ar(C_{2v}).

It is instructive to compare the properties of the C–H bonds of $C_2H_5^+$ with those of C_2H_4 to derive the effects of protonation of the C=C bond on the strength of the adjacent C–H bonds. Calculations predict that protonation induces only a minor elongation of the C–H bonds by 0.0027 Å (1.0802 vs. 1.0829 Å), accompanied by an insignificant change in the average C–H stretching wavenumbers (3052.9 vs. 3053.2 $\mathrm{cm^{-1}}$). These observations are reproduced by the experimental wavenumbers of 3117 (b_1) and 3037 $\mathrm{cm^{-1}}$ (b_2) for $C_2H_5^+\cdot$Ar, which are close to the corresponding wavenumbers of the IR-active modes of C_2H_4 of 3106 (b_{2u}) and 2989 $\mathrm{cm^{-1}}$ (b_{3u}).[2] Apparently, protonation of the C=C bond in ethene has little effect on the adjacent C–H bonds, which remain typical C–H bonds for a C atom with sp^2 hybridization. In contrast, protonation of C_2H_4 significantly destabilizes the C=C bond and induces a bond elongation of about 0.05 Å (1.3298 vs. 1.3784 Å).

In conclusion, Ar-tagging IRPD spectroscopy provided unambiguous evidence that protonated ethene has a nonclassical equilibrium structure **1** with a three-center two-electron bond, in agreement with sophisticated quantum chemical calculations. This experimental result is fundamental to our understanding of the theory of chemical bonding in elementary carbocations. Preliminary spectroscopic data on related $C_2H_5^+{\cdot}L_n$ clusters demonstrate that the subtle energy difference between **1** and **2** sensitively depends on the type of solvent, and solvation-induced switching from the nonclassical to the classical structure occurs as the strength of interaction of L with the C atom increases.

Experimental Section

The IRPD spectrum of weakly bound $C_2H_5^+{\cdot}Ar$ adducts was recorded in a tandem quadrupole mass spectrometer (QMS1/2) coupled to a cluster ion source and an octopole ion trap.[18] $C_2H_5^+{\cdot}Ar$ adducts were generated in a pulsed supersonic molecular-beam expansion of an Ar/CH_4 mixture (10:1, stagnation pressure $p = 6$ bar). $C_2H_5^+$ ions were produced by chemical ionization of CH_4,[1c,16e] and $C_2H_5^+{\cdot}Ar$ adducts were formed by subsequent three-body aggregation reactions. The $C_2H_5^+{\cdot}Ar$ cluster ions were mass-selected by QMS1 and irradiated in the adjacent octopole ion guide with a tunable IR laser pulse (ν_{IR}) generated by an optical parametric oscillator laser system.[18] Resonant vibrational excitation of $C_2H_5^+{\cdot}Ar$ ruptured the weak intermolecular bond [Eq. (1)]. The $C_2H_5^+$ fragment ions were selected by QMS2 and monitored as a function of ν_{IR} to obtain the IRPD spectrum of $C_2H_5^+{\cdot}Ar$. Ab initio calculations were carried out at the MP2/6-311G(2df,2pd) level of theory. Minima were located on the potential-energy surface with correction for basis set superposition error. Harmonic vibrational wavenumbers were scaled by the factor 0.9419.

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[20] Stable **2**·Ar adducts could not be identified. As the energy difference between **2** and **1** significantly exceeds the binding energy of **2**·Ar, all possible **2**·Ar complexes collapse barrierlessly into **1**·Ar isomers. Nonetheless, as the intermolecular interaction in **2**·Ar is also small, the effects of Ar complexation on the IR spectrum of **2** in the C–H stretching region are negligible.

[21] Effects on the nonclassical C–H bond on Ar complexation in **1**·Ar(C_{2v}) are somewhat larger ($\Delta R_{CH} = 0.004$ Å, $\Delta\tilde{\nu}_{CH} = -46$ cm^{-1}); the wavenumber of this ν_{CH} mode (ca. 2200 cm^{-1}) is, however, outside of the spectral range investigated.

[22] The four C–H stretching fundamentals of the C_2H_4 moiety in **1**·Ar(C_{2v}) have wavenumbers of 2995 (b_2), 2999 (a_1), 3101 (a_2), 3117 cm^{-1} (b_1), with IR intensities of 31, 1, 0, and 64 km mol^{-1}, respectively.

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