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# Equilibrium Isotope Effects in Cationic Transition-Metal(I) Ethene Complexes $M(C_2X_4)^+$ with M = Cu, Ag, Au and X = H, D

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Mass spectrometric methods are used to examine the H/D equilibrium isotope effects (EIEs) of cationic $M(C_2X_4)^+$ complexes (X = H, D) of the coinage metals M = Cu, Ag, and Au. Different experimental methods to determine the EIEs are applied, and the best precision is achieved for measurements involving independently prepared mixtures of ethene and [$D_4$]-ethene. In addition, ab initio calculated frequencies are used to derive the corresponding EIEs. In the evaluation of the experimental data as well of the theoretical predictions great care is taken to avoid all possible abberrations and to explicitly treat systematic errors. The measured EIEs of 0.86 ± 0.02 for $Cu(C_2H_4)^+/Cu(C_2D_4)^+$, 0.83 ± 0.02 for $Ag(C_2H_4)^+/Ag(C_2D_4)^+$, and 0.74 ± 0.02 for $Au(C_2H_4)^+/Au(C_2D_4)^+$ in favor of the respective deuterated metal complexes are in complete harmony with computed values of 0.86, 0.83, and 0.74, respectively. Interestingly, for the olefin complexes studied here, the EIEs associated with H/D substitution of ethene are not an appropriate measure for the extent of pyramidalization of the methylene groups of the olefin upon complexation to $M^+$.

## Introduction

Isotopes play an enormous role in the elucidation of thermochemical and kinetic quantities, reaction mechanisms, dynamic effects, etc. They find their most common quantitative expression in the kinetic isotope effect (KIE), which, by definition, is the ratio of rate constants for an unlabeled molecule compared with its heavier variant. Large KIEs occur with hydrogen, deuterium, and tritium because the relative mass differences are most pronounced for these isotopes; these KIEs can be significant provided the reactions are kinetically controlled and cleavage and/or formation of an element−hydrogen bond is actively involved in the rate-determining step(s); exceptions that often result in inverse KIEs are reactions involving isotope discriminating steps after the rate-limiting step as well as processes involving hidden hydrogen atom transfer.[1] In contrast, equilibrium isotope effects (EIEs) are usually much smaller, because substitution by a heavy isotope slows down forward as well as backward reactions such that the overall effects on the equilibrium constants $K_{eq}$ are small. Thus, typical EIEs are close to unity. Notwithstanding, EIEs have nowadays found various applications such as age determination, and geological and environmental imaging.[2] Moreover, the analysis of EIEs can provide detailed insight into bonding mechanisms of species of fundamental interest, such as transition-metal complexes.[3] An essential prerequisite for the analysis of EIEs is, however, the ability to measure isotopic ratios with high precision.

$$M(C_2D_4)^+ + C_2H_4 \rightleftarrows M(C_2H_4)^+ + C_2D_4 \qquad (1)$$

Here, we report measurements of the EIEs associated with the ligand-exchange reaction 1 for the coordination of ethene and [$D_4$]-ethene, respectively, to the “bare” monocations of the coinage metals, copper, silver, and gold,[4] in the highly diluted gas phase ($p < 10^{-7}$ mbar) using ion-cyclotron resonance (ICR) mass spectrometry.[5] In the equilibrium measurements, particular care is taken to achieve maximal accuracy while accounting for

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(2) For a compilation of various aspects, see several articles in the Honour Biography A. O. C. Nier as a special issue of *Int. J. Mass Spectrom. Ion Processes* **1995**, *146/147*, e.g., Riciputi, L. R.; Duckworth, D. C.; Barshick, C. M.; Smith, D. H., p 55, and references therein.

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all apparent statistical as well as systematic errors. Further, the EIEs are calculated using a previously described formalism[6] in conjunction with vibrational frequencies of bare ethene and its $M^+$ complexes as predicted by density functional theory; again, possible shortcomings in the theoretical predictions are explicitly considered. Hence, this paper describes for the first time a detailed analysis of EIEs for an isolated transition-metal complex[7] without involving those interferences which, on principal grounds, cannot be ruled out in condensed-phase experiments.

## Experimental and Theoretical Methods

The experiments were performed with a Spectrospin CMS 47X FTICR mass spectrometer, which has been described elsewhere[8] and has been used in several previous experimental studies of $M(C_2H_4)^+$ complexes (M = Cu, Ag, Au).[9] In brief, $M^+$ cations were generated by laser-desorption/laser-ionization[10] of the corresponding metals in the external ion source of the instrument. The ions were transferred to the analyzer cell which is located within a superconducting magnet (field strength 7.05 T), and the cations of the most abundant isotopes ($^{63}$Cu, $^{107}$Ag, and $^{197}$Au) were mass selected. Even though the $M^+-C_2H_4$ binding energies are significant for the coinage metals,[4] bimolecular association of $M^+$ and ethene is negligible in the highly diluted gas phase ($p < 10^{-7}$ mbar). Therefore, the desired $M(C_2X_4)^+$ ions (X = H, D) were generated by ligand-exchange reactions of $C_2X_4$ with appropriate $M(L)^+$ cations having more weakly bound ligands L, i.e., L = cyclohexane for M = Cu and Ag,[11] L = hexafluorobenzene for M = Au.[9b] The corresponding adduct complexes $Cu(c\text{-}C_6H_{12})^+$, $Ag(c\text{-}C_6H_{12})^+$, and $Au(C_6F_6)^+$ are conveniently formed by reacting the bare metal cations with the pulsed-in ligands. As cyclohexane and hexafluorobenzene have favorable pumping characteristics in high-vacuum devices, these neutrals can be removed from the ICR cell within a few seconds. In the presence of ethene, these $M(L)^+$ complexes readily undergo ligand exchange to afford the corresponding $M(C_2X_4)^+$ complexes (X = H, D). Hence, this gas-phase route via ligand-switching reactions allows a versatile and efficient access to the $M(C_2X_4)^+$ cations of these metals. Subsequently, the ions of interest were mass-selected and then trapped in $C_2H_4/C_2D_4$ mixtures of various compositions for different reaction times (see below). In most cases, $M(C_2H_4)^+$ and $M(C_2D_4)^+$ were mass-selected simultaneously in order to avoid superfluous losses of ion intensity as well as unintentional excitation of the ions of interest upon mass selection. As demonstrated previously, these conditions are ideal to probe ion/molecule reactions occurring at room temperature.[4,9,12] Further, mass discrimination in the detection of $M(C_2H_4)^+$ and $M(C_2D_4)^+$ in the broadband mode is negligible provided that sufficient memory is used in data processing; for example, similar experiments gave isotope patterns for $Au(Xe)^+$ and $Au(Xe)_2^+$ cations which were accurate within less than ±2% of the natural abundances.[13] All operations including data accumulation and processing were performed using an ASPECT 3000 minicomputer connected to a personal computer running under Windows NT.

For the experimental evaluation of the EIEs, the equilibrium of reaction 1 was studied by introducing both $C_2H_4$ and $C_2D_4$ simultaneously while monitoring the intensities of $M(C_2H_4)^+$ and $M(C_2D_4)^+$ at various reaction times and pressures. Equilibria were assumed to be established when the variations of the $M(C_2D_4)^+/M(C_2H_4)^+$ ratios with time reached statistical fluctuations. Note that at the pressure conditions used, association reactions of the monoligated metal(I) complexes $M(C_2X_4)^+$ with the neutral ethenes to form the corresponding bisligated complexes $M(C_2X_4)_2^+$ were negligible (see below). The experimentally observed ion intensities of $M(C_2X_4)^+$ were corrected for the noise level as well as contributions arising from the natural abundance of $^{13}$C and incomplete deuterium incorporation in the labeled ethenes; note that these corrections are nonnegligible in the determination of EIEs. The corrected $M(C_2D_4)^+/M(C_2H_4)^+$ ratios were used in conjunction with the partial pressures $p(C_2H_4)$ and $p(C_2D_4)$ to determine the equilibrium constants ($K_{eq}$), from which the changes in free energies may be deduced using the Gibbs−Helmholtz equation $\Delta\Delta G = -RT \ln K_{eq}$ assuming $T = 298$ K; note that for reaction 1 $K_{eq}$ is equal to EIE by definition.

Ethene (99.995%) was purchased from Linde, Germany. [*E*-1,2-$D_2$]-ethene (>98 atom % D) and [$D_4$]-ethene (>99 atom % D) were obtained from C/D/N Isotopes, Canada. These gases were used without further purification. Preparation of the ethene mixtures by gas volumetry employed a stainless steel apparatus equipped with a manometer (Vacubrand, Germany) and vacuum-tight vessels of known volumes of about 800 mL. Typical operating pressures were on the order of 100 mbar. Under these conditions, it is reasonable to assume that the response of the manometer to $C_2H_4$, $C_2H_2D_2$, and $C_2D_4$ is identical in that the ethenes behave as ideal gases with respect to deuteration. The accuracy of the gas volumetric mixing is estimated as ±0.5% per component, and the correctness of the mixtures was further ensured by gas gravimetry (±1% per component).

In analogy with our previous computational studies of $M(C_2H_4)^+$ complexes of the coinage metals,[4,14] we have used density functional theory for the frequency calculations.[15] Specifically, Becke's three-parameter fit[16] in conjunction with the correlation functional developed by Lee, Yang, and Parr[17] (B3LYP) was used. In this study, we employed this method together with the option ‘finegrid’ as implemented in the Mulliken program;[18] this is referred to as MB3LYP. Relativistic effects were accounted for by using the ECP_QD95 pseudopotentials of Stevens et al.[19] for the coinage metals; D95* basis sets[20] were used for carbon and hydrogen. The calculated structures of $M(C_2H_4)^+$ were in perfect agreement with the previously reported ones.[4]

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[7] For examples of EIE determinations for transition-metal complexes using other techniques, see: Stöckigt, D.; Hrušák, J.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1995**, *149/150*, 1. (b) L. C.-Y.; Chen, Q.; Chen, H.; Freiser, B. S. *Int. J. Mass Spectrom. Ion Processes* **1997**, *167/168*, 713.

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## Results

Kinetic isotope effects are defined as the ratios of the rate constants for the reactions of substrates with light and the heavy isotopes, e.g., KIE $= k_H/k_D$ for hydrogen and deuterium. Usually, $k_H$ exceeds $k_D$ such that "normal" KIEs results. Because we consider equilibrium isotope effects in coordination of ethene to $M^+$, the nature of the EIEs associated with reaction 1 as being classified "normal" or "inverse" is a matter of definition; conventionally they are referred to as "inverse" when labeled ethene is more strongly bound to the metal cation than the unlabeled one.[6,21] This kind of "inverse" EIEs, resulting in $K_{eq} < 1$ for eq 1, are also found for the $M(C_2X_4)^+$ complexes of the coinage metals under study. Further, we note in passing that our previous computational studies of the $M(C_2H_4)^+$ cations predicted bond-dissociation energies of $D_0(Cu^+{-}C_2H_4) = 48 \pm 3$ kcal/mol, $D_0(Ag^+{-}C_2H_4) = 34 \pm 2$ kcal/mol, and $D_0(Au^+{-}C_2H_4) = 65 \pm 3$ kcal/mol.[4,22] These binding energies are well above those typical for mere electrostatic interactions, and the metal–olefin complexes can thus be described as tightly bound systems. Nevertheless, the bonding schemes differ greatly for M = Cu, Ag, and Au.[4] Thus, while $Ag(C_2H_4)^+$ is a T-shaped molecule with mostly electrostatic interaction, $Au(C_2H_4)^+$ is best described as a metallacyclopropane, and the binding situation in $Cu(C_2H_4)^+$ is between these two extremes. These differences are reflected in the degree of pyramidalization of the methylene groups expressed by the $H_2CC$ dihedral angles, i.e., 180° in free ethene compared to 167.9° in $Cu(C_2H_4)^+$, 169.8° in $Ag(C_2H_4)^+$, and 163.2° in $Au(C_2H_4)^+$, respectively, for the CCSD(T)-optimized structures.[4] These trends in the bonding features among the coinage metals as well as the large variation in bond-dissociation energies in these archetypical Dewar–Chatt–Duncanson complexes were also a major motivation in comparing these $M(C_2H_4)^+$ complexes (M = Cu, Ag, Au) in the present study.

**Computed EIEs.** Harmonic vibrational frequencies of free and complexed ethene and [D$_4$]-ethene were calculated at the MB3LYP level of theory implemented in the Mulliken program.[18] Because ethene is a simple molecule, its vibrational frequencies are quite well known. Despite ongoing refinement of some modes,[23] throughout this paper we refer to the comprehensive compilation of ethene frequencies due to Duncan and Hamilton.[24] Comparison of the experimental frequencies of $C_2H_4$ and $C_2D_4$ with the data computed with MB3LYP yields a uniform scaling factor of 0.968 ± 0.022 for calculated vibrational frequencies $\nu_{calc}$. Similarly, linear regression of experimental and computed values gives $\nu = \nu_{calc}\,(0.995 - 0.126\nu_{calc}/1000\ \text{cm}^{-1})$. These approaches are referred to as uniform and linear scaling further below. Scaling factors close to unity are quite common for density functional methods.[15,25]

The approach to derive EIEs from the calculated frequencies has been outlined previously,[6] and we restrict ourselves to the essentials that are required in the present context. Thus, the EIE of the isotopic exchange reaction 1 can be calculated using eq 2 from the contributions due to mass and momentum terms (MMI), vibrational excitation at room temperature (EXC), and the mere effect of zero-point energy (ZPE), as defined in eqs 3–5.

$$\text{EIE} = \text{MMI} \times \text{EXC} \times \text{ZPE} \tag{2}$$

$$\text{MMI} = \left(\frac{Q_{tr}^{A*}Q_{rot}^{A*}}{Q_{tr}^{A}Q_{rot}^{A}}\right)\left(\frac{Q_{tr}^{B}Q_{rot}^{B}}{Q_{tr}^{B*}Q_{rot}^{B*}}\right) \tag{3}$$

$$\text{EXC} = \frac{\prod_{i}^{3N_r-6} \dfrac{1-e^{-(h\nu_i^{A}/kT)}}{1-e^{-(h\nu_i^{A*}/kT)}}}{\prod_{j}^{3N_p-6} \dfrac{1-e^{-(h\nu_j^{B}/kT)}}{1-e^{-(h\nu_j^{B*}/kT)}}} \tag{4}$$

$$\text{ZPE} = \frac{\prod_{i}^{3N_r-6} \dfrac{e^{(h\nu_i^{A}/2kT)}}{e^{(h\nu_i^{A*}/2kT)}}}{\prod_{j}^{3N_p-6} \dfrac{e^{(h\nu_j^{B}/2kT)}}{e^{(h\nu_j^{B*}/2kT)}}} \tag{5}$$

Here, $Q_{trans}$ and $Q_{rot}$ are the translational and rotational partition functions, $\nu$ is the respective vibrational frequencies, A refers to free $C_2H_4$ and A* to $C_2D_4$, and B refers to the $M(C_2H_4)^+$ complex and B* to $M(C_2D_4)^+$. Further, the MMI term can be approximated by the Teller–Redlich product rule as vibrational product (VP) according to eq 6. For the sake of variability in subsequent modifications, we prefer this replacement and use VP instead of MMI throughout; we note in passing that the computed MMI and VP terms agree within <1%.

$$\text{VP} = \frac{\prod_{i}^{3N_r-6} \dfrac{\nu_i^{A*}}{\nu_i^{A}}}{\prod_{j}^{3N_p-6} \dfrac{\nu_j^{B*}}{\nu_j^{B}}} = \left(\frac{Q_{tr}^{A*}Q_{rot}^{A*}}{Q_{tr}^{A}Q_{rot}^{A}}\right)\left(\frac{Q_{tr}^{B}Q_{rot}^{B}}{Q_{tr}^{B*}Q_{rot}^{B*}}\right) \tag{6}$$

Having established this framework, we can use the calculated frequencies to derive the EIEs associated with reaction 1 for M = Cu, Ag, and Au. For all metals, inverse EIEs are predicted by theory, and these become more pronounced from Cu to Au (Table 1). Further, the VP terms are >1 and quite similar for the three metals, while EXC and ZPE are <1 with a tendency to decrease for the heavier elements. It is obvious from a comparison of the computational results that scaling has a minor influence on the resulting EIEs.[26]

Further, we calculated the contributions of the individual modes to the EIE using the symmetry-correlated

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[21] Wolfsberg, M. *Acc. Chem. Res.* **1972**, *5*, 225.

[22] (a) Here, we use the average of the CCSD(T) and B3LYP data given in ref 4. (b) Experimental values: $D_0(Cu^+{-}C_2H_4) = 41.5$ kcal/mol (Sievers, M. R.; Jarvis, L. M.; Armentrout, P. B. *J. Am. Chem. Soc.* **1998**, *120*, 1891), $D_0(Ag^+{-}C_2H_4) = 33.7$ kcal/mol (Guo, B. C.; Castleman, A. W., Jr. *Chem. Phys. Lett.* **1991**, *181*, 16), $D_0(Au^+{-}C_2H_4) \approx 65$ kcal/mol (refs 9b and 13).

[23] For a recent example, see: Bach, M.; Georges, Hepp, M.; Herman, M. *Chem. Phys. Lett.* **1998**, *294*, 533.

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[25] Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

[26] This statement is by no means general. Probably, the low sensitivity of the computed EIEs toward scaling is due to the fact that the scaling schemes are anyhow close to unity.

**Table 1. Calculated EIEs and Their Components for Reaction 1 with the Given Metals and Different Methods for Scaling of the Calculated Frequencies**[a]

| metal M | scaling[b] | VP | EXC | ZPE | EIE |
|---|---|---|---|---|---|
| Cu | none | 1.654 | 0.842 | 0.614 | 0.855 |
| | uniform | 1.654 | 0.837 | 0.623 | 0.862 |
| | linear | 1.650 | 0.841 | 0.616 | 0.855 |
| Ag | none | 1.690 | 0.817 | 0.600 | 0.827 |
| | uniform | 1.690 | 0.812 | 0.610 | 0.837 |
| | linear | 1.685 | 0.816 | 0.606 | 0.833 |
| Au | none | 1.697 | 0.877 | 0.496 | 0.738 |
| | uniform | 1.697 | 0.871 | 0.508 | 0.750 |
| | linear | 1.691 | 0.875 | 0.504 | 0.746 |

[a] See text for definition of the different contributions to the EIE. [b]No scaling of the calculated frequencies, uniform scaling with a scaling factor of 0.968, and scaling according to linear regression using $\nu = \nu_{calc}$ $(0.995 - 0.126\nu_{calc}/1000\ cm^{-1})$.

approach previously described.[6] In this treatment a one-to-one correlation between the modes of free and bound ethene is made, using established point-group correlation rules.[6] The individual EIE contributions of most frequencies (Table 2) are close to unity; major contributors to the overall EIEs are $\nu_3$, $\nu_5$, and $\nu_{11}$, which are associated with inverse EIEs, and $\nu_9$, which is larger than unity (Figure 1a). However, the modes $\nu_6$, $\nu_9$, and $\nu_{11}$ are all of same symmetry (irreducible representation $a_1$ in $C_{2v}$ point-group symmetry) and are, unlike the other modes, so extensively coupled that the individual contributions of these modes to the EIEs are less meaningful.[27] Indeed, these three $a_1$ modes cannot be factored separately and should therefore only be considered together: the products of the contributions to the EIEs from the three coupled modes are small and inverse for the three coinage metal complexes (0.988 for Cu, 0.978 for Ag, and 0.984 for Au).

With respect to the computed relative isotopic shifts $\Delta\nu_{i,rel} = [\nu_i(M(C_2H_4)^+) - \nu_i(M(C_2D_4)^+)]/\nu_i(M(C_2H_4)^+)$, consideration of those modes (Figure 1b) that show variations between the metals and/or have previously been reported to affect the EIEs in olefin complexation is instructive.[6] Consistent with the different binding situations of the cationic ethene complexes of the coinage metals mentioned above, none of the modes displayed in Figures 1a and 1b shows a linear trend from Cu to Au (except those that are hardly affected, of course). Due to the coupling of modes $\nu_6$, $\nu_9$, and $\nu_{11}$, the net effect of these $a_1$ modes is again rather small, and we are left with the modes $\nu_1$, $\nu_3$, and $\nu_5$, none of which has a pronounced effect, however. It is particularly noteworthy that the $b_2$-symmetrical ethene-twist mode $\nu_3$ (or metal−ligand wagging mode) correctly correlates with the extent of pyramidalization of the carbon atoms, but fails to correlate with the overall EIEs. While chemical intuition may suggest that the EIE should correlate with the extent of olefin rehydridization, this is obviously *not* the case in these coinage metal compounds which can indeed be considered as prototype olefin complexes.

**Experimental EIEs.** Our first approach to the experimental determination of the EIEs associated with reaction 1 applied conventional methods of ICR mass spectrometry for determining thermochemical equilibria.[28] In this approach (method I), some other transition metals were examined besides the coinage metals. The equilibrium constants $K_{eq}$ and thus the EIEs were derived from the partial pressures of ethene, $p[C_2H_4]$, and $[D_4]$-ethene, $p[C_2D_4]$, as well as the relative abundances of the corresponding olefin complexes, $I[M(C_2H_4)^+]$ and $I[M(C_2D_4)^+]$ using eq 7.

$$\mathrm{EIE} = K_{eq} = \frac{I[M(C_2H_4)^+]p(C_2D_4)}{I[M(C_2D_4)^+]p(C_2H_4)} \tag{7}$$

To determine $I[M(C_2H_4)^+]$ and $I[M(C_2D_4)^+]$ under equilibrium conditions, the isolated ethylene complexes were trapped in the cell until constant intensity ratios were established (usually after 15−20 s). This ratio was measured for at least three different trapping times (e.g., 20, 30, and 40 s), and spectra were accumulated until signal-to-noise ratios ≥ 200 were achieved. This procedure was repeated for three different pressure ratios (e.g., ca. 4:1, 1:1, and 1:4), and the reported EIEs are the resulting averages (Table 3). The relative pressures of both ethenes were derived from the ion gauge readings as well as the intensities of the corresponding molecular ions upon electron ionization inside the ICR cell using electrons of 12 eV kinetic energy.

Inspection of Table 3 reveals that complexation of $M^+$ with ethene is associated with inverse EIEs for all metals studied; this is consistent with the above computational predictions for the coinage metals. However, it is also obvious that the accuracy of the experimental data is by no means satisfactory. In fact, nothing more but a qualitative comparison with theory can be made, because already the statistical error margins of the experimental figures are simply too large; so far, systematic errors are not even considered (see below). Examination of the experimental parameters reveals that the major source of error is due to the determination of the partial pressures of the two ethenes in the $10^{-8}$ mbar regime. Specifically, the ion-gauge reading has a maximal precision of about 2%, the sensitivities of the gauge may slightly differ for $C_2H_4$ and $C_2D_4$,[29] and during the experiments, pressure is only measured as the sum of $p(C_2H_4)$ and $p(C_2D_4)$. Therefore, even slight drifts of the leak valves used for introduction of the two gases during the time required to perform a complete set of experiments (ca. 2 h per metal) lead to variations of the pressure ratios $p(C_2H_4)/p(C_2D_4)$, which significantly affect the precision of the measured EIEs. While the achievable precision using this approach is entirely sufficient in normal equilibrium measurements,[28] for example, in terms of thermochemical bracketing the EIEs correspond to $\Delta\Delta_RG_{298}$ of less than 0.2 kcal/mol, it is insufficient for an accurate quantification of the small differences caused by the EIEs associated with reaction 1.

To circumvent the problems associated with the pressure measurements, we pursued another strategy

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(27) Modes $\nu_6$, $\nu_9$, and $\nu_{11}$ correspond to the symmetric out-of-plane wag, the symmetric deformation (scissors) mode, and the C−C stretch, respectively. Quantum mechanical coupling between $a_1$ symmetry modes for metal−ethene complexes has a long history and has led to considerable confusion, the assignment of $\nu_{CC}$ in particular. As an indication of mode coupling, we note that the products of all three H/D frequency ratios are 1.95 for Cu−Au, i.e., close to the expected value of 2.0 if only two of the three modes are formally deuterium sensitive.

(28) Bouchoux, G.; Salpin, J. Y.; Leblanc, D. *Int. J. Mass Spectrom. Ion Processes* **1996**, *153*, 37.

(29) For example, the ion-gauge sensitivities for $H_2$ and $D_2$ differ by about 10%, see: Nakao, F. *Vacuum* **1975**, *25*, 431.

**Table 2. EIEs Calculated[a] for the Individual Modes of the $M(C_2X_4)^+$ Complexes[b]**

| $\nu_i$[c] | | $Cu(C_2H_4)^+$ | $Cu(C_2D_4)^+$ | EIE | $Ag(C_2H_4)^+$ | $Ag(C_2D_4)^+$ | EIE | $Au(C_2H_4)^+$ | $Au(C_2D_4)^+$ | EIE |
|---|---|---|---|---|---|---|---|---|---|---|
| $\nu_1$ | $b_1$ | 273.0 | 246.1 | 0.987 | 226.8 | 202.9 | 0.990 | 326.7 | 297.7 | 0.984 |
| $\nu_2$ | $a_1$ | 325.4 | 311.3 | 0.992 | 243.9 | 232.2 | 0.995 | 328.6 | 313.0 | 0.991 |
| $\nu_3$ | $b_2$ | 480.2 | 347.5 | 0.907 | 443.4 | 318.5 | 0.918 | 619.6 | 446.0 | 0.854 |
| $\nu_4$ | $b_2$ | 831.1 | 597.2 | 1.006 | 833.0 | 598.6 | 1.005 | 833.6 | 599.2 | 1.004 |
| $\nu_5$ | $b_1$ | 1021.4 | 821.8 | 0.950 | 1026.2 | 825.6 | 0.948 | 1057.2 | 837.1 | 0.920 |
| $\nu_6$ | $a_1$ | 1058.0 | 797.0 | 0.952 | 1063.7 | 799.9 | 0.948 | 1077.7 | 804.9 | 0.934 |
| $\nu_7$ | $a_2$ | 1036.3 | 734.3 | 1.010 | 1051.5 | 744.4 | 1.000 | 1003.8 | 712.0 | 1.031 |
| $\nu_8$ | $a_2$ | 1224.7 | 988.4 | 0.992 | 1231.6 | 995.8 | 0.992 | 1222.2 | 982.5 | 0.988 |
| $\nu_9$ | $a_1$ | 1310.8 | 993.6 | 1.097 | 1327.2 | 995.7 | 1.072 | 1266.4 | 983.5 | 1.160 |
| $\nu_{10}$ | $b_1$ | 1460.4 | 1082.9 | 1.005 | 1468.2 | 1087.7 | 0.999 | 1468.0 | 1087.2 | 0.999 |
| $\nu_{11}$ | $a_1$ | 1591.8 | 1434.7 | 0.946 | 1603.7 | 1456.8 | 0.962 | 1565.4 | 1381.4 | 0.908 |
| $\nu_{12}$ | $b_1$ | 3124.9 | 2256.9 | 1.012 | 3145.5 | 2272.3 | 1.001 | 3138.0 | 2266.9 | 1.005 |
| $\nu_{13}$ | $a_1$ | 3138.5 | 2306.1 | 0.984 | 3144.1 | 2314.8 | 0.990 | 3156.2 | 2312.0 | 0.962 |
| $\nu_{14}$ | $a_2$ | 3228.8 | 2415.1 | 1.010 | 3236.5 | 2420.4 | 1.006 | 3247.2 | 2429.6 | 1.002 |
| $\nu_{15}$ | $b_2$ | 3247.7 | 2418.0 | 1.007 | 3257.9 | 2426.1 | 1.002 | 3264.2 | 2431.2 | 1.000 |
| product | | | | 0.855 | | | 0.833 | | | 0.746 |

[a] In this particular example, the linear scaling method (see Table 1) was used in the evaluation of the EIEs. [b]Calculated frequencies ($cm^{-1}$) of free $C_2H_4$: 841.7, 956.7, 968.7, 1050.1, 1233.4, 1378.4, 1466.8, 1686.3, 3145.2, 3165.0, 3229.2, 3260.0. Calculated frequencies ($cm^{-1}$) of free $C_2D_4$: 605.0, 790.6, 732.8, 742.8, 1003.5, 1004.5, 1086.8, 1565.1, 2271.5, 2341.9, 2409.9, 2427.0. [c]Frequencies are numbered according to increasing $cm^{-1}$ for $Cu(C_2H_4)^+$ and were correlated with those of free ethene as described in ref 6.

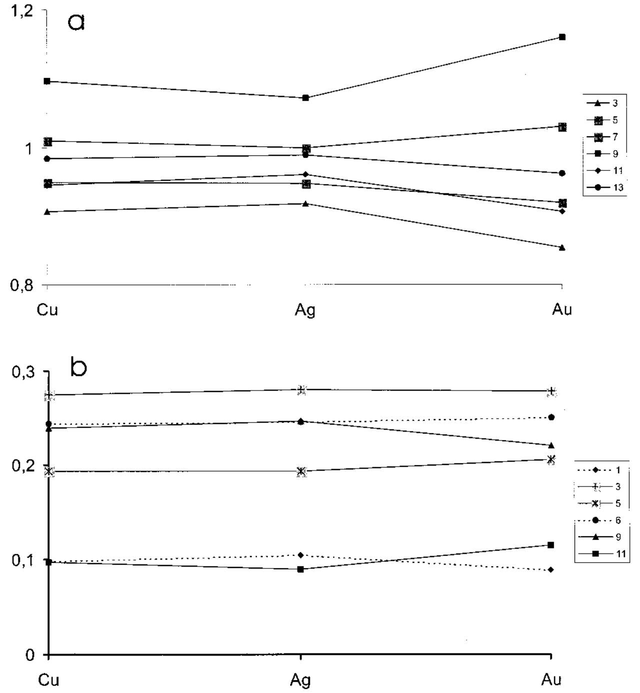

**Figure 1.** (a) Contributions of the selected modes $\nu_i$ to the computed EIEs in $M(C_2X_4)^+$ complexes (X = H, D) for M = Cu, Ag, and Au. For the sake of clarity, only the most sensitive modes are displayed (see Table 2). (b) Relative isotopic shifts $\Delta\nu_{i,\mathrm{rel}}$ of selected modes $\nu_i$ in $M(C_2H_4)^+$ and $M(C_2D_4)^+$ complexes for M = Cu, Ag, and Au; see text and Table 2.

**Table 3. Experimental EIEs of $M(C_2X_4)^+$ Complexes Determined for Monocations of Various Metals M Using Method I[a]**

| M | EIE |
|---|---|
| Fe | 0.86 ± 0.07 |
| Co | 0.92 ± 0.06 |
| Ni | 0.83 ± 0.08 |
| Pd | 0.98 ± 0.06 |
| Cu | 0.97 ± 0.07 |
| Ag | 0.86 ± 0.07 |
| Au | 0.82 ± 0.08 |

[a] Preparation of $M(C_2X_4)^+$ complexes by reactions of $M^+$ with propane (M = Fe − Ni), chloroethane (M = Pd), cyclohexane (M = Cu, Ag), and hexafluorobenzene (M = Au), see ref 5.

(method II). Thus, gas volumetry was used to prepare well-defined mixtures of ethenes with an accuracy of ±0.5% for each of the components.[30] Trapping of mass-selected $M(C_2H_4)^+$ and $M(C_2D_4)^+$ ions in such mixtures affords ligand exchange, and the $M(C_2H_4)^+/M(C_2D_4)^+$ ratios are by definition independent of the absolute pressures once equilibria are established, provided that termolecular reactions do not interfer.[31,32] Again, the $M(C_2H_4)^+/M(C_2D_4)^+$ ratios have been determined at various reaction times, and different overall pressures for which no systematic variations were found.[33] The results obtained with method II agree with those of method I, while having a significantly improved accuracy (Table 4). A ternary mixture containing ethene, [*E*-1,2-$D_2$]-ethene, and [$D_4$]-ethene[30] was examined in the same manner.

Unless a sophisticated setup is used, a disadvantage of method II is the costs because reasonably accurate gas volumetry requires ambient pressures and volumes and thus a significant amount of the labeled compounds. For example, we used partial pressures of about 100 mbar and volumes of about 800 mL in the preparation of the gas mixtures; this corresponds to a consumption of ca. 100 mg of labeled ethenes in the preparation of mixtures which can hardly be used for other purposes than the determination of EIEs. Nevertheless, significant improvement in accuracy appears worth the costs of preparing these two mixtures.

Despite the increase in accuracy, the measured effects are still too small to allow for a very accurate determi-

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(30) Mixing ratios according to gas volumetry. Binary mixture: $C_2H_4$:$C_2D_4$ = (52.5 ± 0.5):(47.5 ± 0.5). Ternary mixture: $C_2H_4$:*E*-$C_2H_2D_2$:$C_2D_4$ = (41.5 ± 0.5):(27.0 ± 0.5):(31.5 ± 0.5).

(31) In the $10^{-8}$ mbar regime examined here, the formation of the bisligated $M(C_2H_4)_2^+$ complexes occurs about 50 times slower than ligand exchange. Exact quantification would require pressure-dependent studies because $M(C_2H_4)_2^+$ formation occurs via termolecular processes; see ref 32.

(32) An average three-body rate constant of 3.9 × $10^{-26}$ $cm^6$ $molecules^{-2}$ $s^{-1}$ has been reported for the association of $Au^+$ and $C_2H_4$ at helium pressures of about 0.5 mbar; see: Taylor, W. S.; Campbell, A. S.; Barnas, D. F.; Babcock, L. M.; Linder, C. B. *J. Phys. Chem. A* **1997**, *101*, 2654.

(33) At short reaction times, formation of $M(C_2H_4)^+$ is preferred over that of $M(C_2D_4)^+$ because the collision rate of the unlabeled ethene is larger than that of $C_2D_4$. However, this manifestation of a secondary kinetic isotope effect was not pursued any further.

**Table 4. Experimental EIEs of $M(C_2X_4)^+$ Complexes Determined for M = Cu, Ag, and Au Using Method II**

| | EIE | Cu | Ag | Au |
|---|---|---|---|---|
| binary mixture[30]<br>$C_2H_4/C_2D_4$ | $M(C_2H_4)^+/M(C_2D_4)^+$ | 0.92 ± 0.02 | 0.89 ± 0.02 | 0.79 ± 0.02 |
| ternary mixture[30]<br>$C_2H_4$/*E*-$C_2H_2D_2/C_2D_4$ | $M(C_2H_4)^+/M(C_2H_2D_2)^+$ | 0.98 ± 0.03 | 0.95 ± 0.03 | 0.88 ± 0.03 |
| | $M(C_2H_2D_2)^+/M(C_2D_4)^+$ | 0.95 ± 0.03 | 0.92 ± 0.03 | 0.91 ± 0.03 |
| | $M(C_2H_4)^+/M(C_2D_4)^+$ | 0.93 ± 0.03 | 0.88 ± 0.03 | 0.81 ± 0.03 |

nation of the differential EIEs associated with partially labeled ethenes. Thus, while the EIEs associated with [*E*-1,2-$D_2$]-ethene are clearly between those observed for $C_2H_4/C_2D_4$, regarding the experimental error margins, a rigorous quantitative comparison with computed values for partially labeled ethenes does not appear worth the effort. In particular, we therefore restricted ourselves to the ternary mixture containing [*E*-1,2-$D_2$]-ethene and did not include other isotopomers such as [*Z*-1,2-$D_2$]- and [1,1-$D_2$]-ethene. Nevertheless, the EIEs associated with reaction 1 as derived from the experimental data obtained with the ternary mixture nicely confirm those obtained for the binary $C_2H_4/C_2D_4$ system (Table 4).

Before continuing with the discussion, let us briefly address some possible systematic errors in the determination of the EIEs; others are to be addressed below. Common to methods I and II is that the EIEs could systematically differ from the true values due to mass discrimination in the determination of the intensities of $M(C_2H_4)^+$ and $M(C_2D_4)^+$. However, the masses of the ethene complexes hardly differ (91 and 95 amu for $^{63}$Cu, 135 and 139 amu for $^{107}$Ag, and 225 and 229 amu for $^{197}$Au). Provided that the computer memory in data processing is sufficient, mass discrimination is therefore neglected; this conclusion is supported by the fact that the same approach accurately reproduces the calculated isotope patterns of $Au(Xe)^+$ and $Au(Xe)_2{}^+$ complexes.[13] Another possible perturbation could be due to rapid associations of the $M(C_2X_4)^+$ ions with ethene to the corresponding bisligated complexes $M(C_2H_4)_2{}^+$, $M(C_2H_4)(C_2D_4)^+$, and $M(C_2D_4)_2{}^+$. Association reactions and/or side reactions may alter the $M(C_2H_4)^+/M(C_2D_4)^+$ ratios from the true EIEs to some steady-state values if the rate constants for association of another ligand molecule differ for the isotopic variants.[13] The latter assumption is quite reasonable because the deuterated variants have significantly increased densities of states due to the lower frequencies with deuterium. Nevertheless, kinetic measurements reveal that upon trapping of mass-selected $M(C_2D_4)^+$ in pure $C_2H_4$ ligand exchange occurs rapidly, i.e., about 40% of the collision rate for all three metals compared to 50% for thermoneutral ligand exchange,[34] while association to the bisligated complexes is negligible.[31]

**Table 5. Comparison of Calculated and Experimental EIEs Using Different Approaches; See Text for Further Details**

| | | Cu | Ag | Au |
|---|---|---|---|---|
| | | Experiment | | |
| 1 | method I[a] | 0.97 ± 0.07 | 0.86 ± 0.07 | 0.82 ± 0.08 |
| 2 | method II, binary mixture[b] | 0.92 ± 0.02 | 0.89 ± 0.02 | 0.79 ± 0.02 |
| 3 | method II, ternary mixture[b] | 0.93 ± 0.03 | 0.88 ± 0.03 | 0.81 ± 0.03 |
| 4 | Knudsen diffusion[c] | 0.86 ± 0.02 | 0.83 ± 0.02 | 0.74 ± 0.02 |
| | | Theory | | |
| 5 | no scaling[d] | 0.855 | 0.827 | 0.738 |
| 6 | uniform scaling[d] | 0.862 | 0.837 | 0.750 |
| 7 | linear scaling[d] | 0.855 | 0.833 | 0.746 |
| 8 | hot (373 K)[e] | 0.905 | 0.885 | 0.820 |
| 9 | hot (473 K)[e] | 0.941 | 0.924 | 0.879 |
| 10 | low frequency offset (−20%)[f] | 0.891 | 0.863 | 0.794 |
| 11 | differential scaling (0.995)[g] | 0.909 | 0.885 | 0.794 |

[a] Experimental data from Table 3. [b] Experimental data from Table 4. [c] Values from row 2 multiplied with $\sqrt{m(C_2H_4)/m(C_2D_4)} = 0.935$. [d] Calculated EIEs from Table 1. [e] Values from row 7 converted to effective temperatures of $T$ = 373 and 473 K, respectively. [f] Values from row 7 with a scaling of the low-lying modes $\nu_1$−$\nu_3$ by 0.8. [g] Values from row 7 assuming a slightly different scaling for free (1.0) and complexed (0.995) ethene; see text.

## Discussion

The experimental and theoretical results for the EIEs of the ethene complexes of the coinage metals are summarized in Table 5, which also contains corrected values derived from several assumptions described below. The experimental data obtained with methods I and II (rows 1−3 in Table 5) are consistent with each other and yield, for example, EIEs of 0.92, 0.89, and 0.79 for M = Cu, Ag, and Au (row 2 in Table 5). The theoretical data are insensitive with respect to different methods used for scaling of the vibrational frequencies, and their averages predict EIEs of 0.86, 0.83, and 0.74 for M = Cu, Ag, and Au (rows 5−7 in Table 5). Hence, the computed EIEs are consistently lower than the measured values; the ratios of computed and measured EIEs are 0.93 for copper as well as silver and 0.94 for gold. Thus, experiment and theory agree upon the *relative* EIEs for the coinage metals, but disagree upon the *absolute* EIEs. This congruence between experimental and theoretical EIE ratios is temperature dependent; thus, the calculated relative EIEs only match the experimental ratios at a temperature of 298 K (column 1 versus column 3 in Table 6). At higher and lower temperatures, the calculated ratios deviate significantly from the experimental ones. The observation that the absolute EIEs resulting from theory and experiment differ by a constant factor and the temperature dependence strongly implicate the operation of systematic errors, rather than statistical ones.

In addition to the systematic errors addressed above, the experimental determination of the EIEs could be disturbed by two phenomena. The first concerns the

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(34) Measured rate constants when trapping $M(C_2D_4)^+$ in pure $C_2H_4$: 4.3 × $10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for M = Cu, 3.7 × $10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for M = Ag, and 3.8 × $10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for M = Au; these values are to be compared with collision rates of about 1 × $10^{-9}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for these reactions. Note that in the absence of a barrier the maximal rate constant for degenerate ligand exchange is half the collision rate.

**Table 6. Experimentally Determined Relative EIEs for the Cationic Ethene Complexes of the Coinage Metals (M = Cu, Ag, Au) and Theoretical Values Calculated at Four Different Effective Ion Temperatures**

| | experiment[a] | theory (223 K) | theory (298 K) | theory (373 K) | theory (473 K) |
|---|---|---|---|---|---|
| EIE(Ag)/EIE(Cu) | 0.97 ± 0.02 | 0.969 | 0.974 | 0.978 | 0.982 |
| EIE(Ag)/EIE(Au) | 0.89 ± 0.02 | 0.838 | 0.896 | 0.927 | 0.951 |
| EIE(Cu)/EIE(Au) | 0.86 ± 0.02 | 0.812 | 0.872 | 0.906 | 0.934 |

[a] Note that the $C_2H_4/C_2D_4$ mixing ratio, as a main source of the remaining experimental error in the absolute EIEs, cancels in the comparison of relative values.

effective ion temperatures. Thus, if the ions were not equilibrated at room temperature, but rather at a somewhat higher figure, the experimental EIEs would consistently be closer to unity than the computational predictions, as observed upon comparison. However, no single temperature exists that could bring about agreement between experiment and theory. For example, the EIEs computed for an effective temperature of 373 K would fit the experimental data for gold, but still deviate for copper, whereas agreement for the latter is almost reached at 473 K, while the EIE predicted for gold is already too large at this temperature (rows 8 and 9 in Table 5). Moreover, the experimentally found relative EIEs given in Table 6 compare favorably with the values computed for 298 K, while consideration of lower and higher ion temperatures increases divergence. Finally, the experiments themselves give no indications for elevated ion temperatures of either metal cation as the measured EIEs were independent of net pressures and reaction times, once equilibria were established.[33] Therefore, we dispute this option. The second source of systematic error in method II is due to the assumption that the composition of the gas mixture remains unchanged during leakage into a high-vacuum device. However, the pressure difference between the reservoir (ca. 200 mbar) and the mass spectrometer (ca. $10^{-8}$ mbar) is enormous. Therefore, the leak valve may act as a nozzle, which is more easily penetrated by the lighter gas. To a very first approximation, we may assume Knudsen diffusion, according to which the gas flows are proportional to the square roots of the masses.[35] This would assume that demixing occurs upon introduction of the $C_2H_4/C_2D_4$ mixture from the reservoir into the ICR in that the heavier isotopologue $C_2D_4$ is slightly discriminated against.[36] Interestingly, inclusion of Knudsen diffusion lowers the EIEs by 0.935, i.e., precisely the factor required to bring about agreement of experiment and theory.

As with experiment, the theoretical approach has two major sources of possible systematic errors. The first concerns anharmonicity of the vibrational modes. While we cannot incorporate anharmonicity explicitly in this study, the possible effects may be roughly estimated by application of an arbitrary offset to the low-lying modes associated with the metal−ligand binding. Row 10 of Table 5 shows an example, in which the associated modes $\nu_1-\nu_3$ of $M(C_2X_4)^+$ were deliberately lowered by 20%. By such, agreement is achieved for M = Au, but the EIEs of the two other metals would still require even larger offsets. While we cannot explicitly address this effect, we do not expect anharmonicity to cause such strong red shifts of the low-lying modes. The second variation, however, even though much more subtle, brings about perfect agreement between experiment and theory. Let us assume that the theoretical descriptions of the isotopic ethene units slightly differ for the free and the complexed molecules in that differential scaling factors apply. In fact, even the very minor change using a differential scaling factor of $f = 0.995$ for the $M(C_2X_4)^+$ frequencies merges the theoretical predictions with the experimental data (row 11 versus 3 in Table 5), primarily due to changes in the ZPE terms. Although it is, of course, quite conceivable that a given level of theory describes free and complexed ethene differently, this effect is likely to compensate in the evaluation of the EIEs in which the relative effects of protio- versus deuterio-variants are considered. It needs to be pointed out, however, that the computational predictions are rather sensitive to differential scaling factors for free and complexed ligands.

Summarizing the discussion of these systematic effects, we chose to correct the experimental EIEs for Knudsen diffusion, thereby reaching almost perfect agreement between experiment and theory (row 4 versus 5−7 in Table 5). The values determined with method I reach the error margins of the EIEs obtained with the Knudsen correction. We attribute this minor divergence to systematic errors operative in the determination of the partial pressures of the ethenes in method I, different sensitivities of the ion gauge for the labeled gases, in particular.[29]

Finally, let us consider the contributions of the separate modes to the EIEs. In the previous analysis of the binuclear $Os_2(CO)_8(C_2X_4)$ cluster (X = H, D), the metal−ligand wagging mode (here, $\nu_3$) was identified as the major source of the EIE associated with ethene binding. This analysis assumed a symmetry correlation between the free rotation of ethene about its C−C bond and the $b_2$ symmetrical torsion of the $CH_2$ planes in the complex as outlined in ref 6. This idea had precedent in Strausz's analysis of the KIEs associated with the addition of atomic sulfur to ethene in the gas phase;[37] the same concept has been recently invoked in the analysis of KIEs in the bromination of ethene.[38] Our results on the $M(C_2X_4)^+$ complexes concur that $\nu_3$ is a major source of the inverse EIEs associated with reaction 1 for the coinage metal cations: binding of the ethene rotational mode incurs enough new vibrational zero-point energy to exceed the difference in zero-point energy for changes in any preexisting modes. However, this simplified analysis of a single mode fails to predict the correct relative EIEs for the coinage metals. More-

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(35) Grassmann, P. *Physikalische Grundlagen der Verfahrenstechnik*, 3rd ed.; Salle & Sauerländer: Frankfurt/M., 1983.

(36) Notwithstanding, it is safe to neglect demixing in the container, because the effective gas flow into the ICR mass spectrometer is minute compared to the content of the reservoir.

(37) (a) Strausz, O. P.; Safarik, I.; O'Callaghan, W. B.; Gunning, H. E. *J. Am. Chem. Soc.* **1972**, *94*, 1828. (b) Strausz, O. P.; Safarik, I. *J. Phys. Chem.* **1972**, *76*, 3613.

(38) Koerner, T.; Brown, R. S.; Gainsworth, J. L.; Klobukowski, M. *J. Am. Chem. Soc.* **1998**, *120*, 5628.

over, the EIEs do not even correlate with the extent of olefin rehybridization. Hence, a clear-cut separation of the individual modes as contributors to the EIE is difficult in the present case, and the net EIEs do in fact not provide an experimental probe for the different bonding modes of the metal−olefin complexes, which largely differ for Cu, Ag, and Au.[4] Thus, while discontinuous trends from Cu to Au in the different modes are obvious (Figure 1), the net EIEs decrease monotonically from copper to gold.

## Conclusion

Using contemporary experimental and theoretical methods, the equilibrium isotope effects for the coordination of $C_2H_4$ and $C_2D_4$ to the “bare” cations of coinage metals are examined. Consideration of the relative EIEs of the coinage metals further supports the previous statement that these ICR experiments sample 298 K thermochemistry. In the final evaluation of the data, agreement between experiment and theory is extremely good, when Knudsen diffusion is taken into account. In fact, one may ask how such a good match could be obtained considering the sensitivity of the computed EIEs toward differential scaling, neglect of anharmonicity effects, etc. Quite certainly, evaluation of the EIEs benefits from fortuitous error cancellations in comparing labeled and unlabeled systems.

The present results on the cationic ethene complexes of the coinage metals set a benchmark for other experimental studies of EIEs. Of particular interest would be a comparison of the present results with measurements using Cooks’ kinetic method,[39] which offers a convenient approach for much more comprehensive studies including a broader range of metals and olefins and which has also been applied to a few transition-metal complexes.[40] To further increase the value of gas-phase determinations of EIEs, experiments at temperatures lower than 298 K would be beneficial because reduced temperatures would increase the EIEs, thereby possibly allowing the distinction of stereoisomeric olefins via equilibrium methods.

The major conceptual conclusion from the present results is that EIEs do not provide generally valid probes for binding mechanisms of olefins, structural reorganization, the distinction between $sp^2$ and $sp^3$ carbons, and the associated degree of pyramidalization in particular. Thus, while the bonding schemes in $M(C_2H_4)^+$ behave discontinuously from copper to gold,[4] the EIEs are found to decrease monotonically from Cu to Au.

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[39] Cooks, R. G.; Patrick, J. S.; Kotiqaho, T.; McLuckey, S. A. *Mass. Spectrom. Rev.* **1994**, *13*, 287.

[40] Selected examples: (a) McLuckey, A. A.; Schoen, A. E.; Cooks, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 848. (b) Chen, L.-Z.; Miller, J. M. *Org. Mass Spectrom.* **1992**, *27*, 883. (c) Schröder, D.; Schwarz, H. *J. Organomet. Chem.* **1995**, *504*, 123. (d) Ma, S.; Wong, P.; Yang, S. S.; Cooks, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 6010. (e) Schroeter, K.; Wesendrup, R.; Schwarz, H. *Eur. J. Org. Chem.* **1998**, *565*, 5.