

Supplementary Material for Comment on “Role of (NO)₂ Dimer in Reactions of Fe⁺ with NO and NO₂ Studied by ICP-SIFT Mass Spectrometry”

Joshua J. Melko¹, Shaun G. Ard¹, Joseph A. Fournier², Nicholas S. Shuman¹, Jürgen Troe³, and

Albert A. Viggiano^{1*}

¹Air Force Research Laboratory, Space Vehicles Directorate, Kirtland AFB, NM 87117-5776, USA

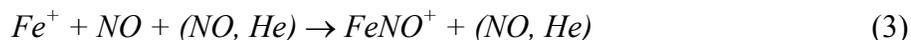
²Sterling Chemistry Laboratory, Yale University, P.O. Box 208107, New Haven, CT 06520, USA

³Institut für Physikalische Chemie, Universität Göttingen, Tammannstrasse 6, D-37077 Göttingen, Germany and Max-Planck-Institut für Biophysikalische Chemie, D-37077 Göttingen, Germany

* Corresponding author: af1.rvborgmailbox@kirtland.af.mil (Albert Viggiano)

Second Order Reaction Mechanism

Bohme 2013 claims that we have misunderstood their proposed three-body mechanism for reaction of Fe⁺ with NO.¹ We presented an analysis of the reaction scheme as follows (reaction numbers are those in Bohme 2013)



Bohme 2013 suggests instead a sequence with the equilibrium of



described by the equilibrium constant K_{eq}^* , and the subsequent reaction



described by the rate constant k_6 . The rate for that process is given by

$$\begin{aligned} \frac{d(\text{products})}{dt} &= k_6 [FeNO^{+*}] [NO] \\ &= k_6 K_{eq}^* [Fe^+] [NO] [NO] \end{aligned}$$

In fact, our analysis focused on (3)-(4) because the rate of that mechanism has a higher upper limit, giving the maximum chance of explaining their data, while we briefly dismissed the more limited (5)-(6) scheme.

The third order rate constant $k_6 K_{eq}^*$ of (5)-(6) is identical with the "strong collision" low pressure rate constant $k_{rec,0}$ previously estimated in our work as $4 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1}$.² Stated another way, in both schemes the rate limiting step is interaction of FeNO^{+*} with a third-body, either stabilization by He, or reaction to products by NO. Assuming each of those processes is 100% efficient, the kinetics are identical and depend on the collision rate with the third-body; i.e. the concentration of the third body. In the experiment, the He buffer is present in $\sim 10^{16} \text{ cm}^{-3}$ while NO is $\sim < 10^{13} \text{ cm}^{-3}$, leading to an upper limit for (3)-(4) that is 10^3 times faster than for (5)-(6). If k_6 is identified with the Langevin collision rate constant for collisions between NO and FeNO^{+*} one should have the maximum possible value for k_6 . That is what was calculated in our work. Even if one would assume that the experimental pressure of 0.35 Torr would correspond exclusively to NO, that would lead to the upper limit of the effective second order rate constant of $5 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ calculated in our article. That is \sim five orders of magnitude smaller than the rate constant reported by the Bohme group. We note here that revised calculations on the bond strength of FeNO^+ , using DFT with the B3LYP functional and the 6-311+G(d) basis set, put the bond energy at approximately 2.11 eV for a triplet structure of FeNO^+ relative to quartet Fe^+ . (We thank the reviewers for this helpful suggestion.) This triplet structure would be spin-allowed if the low-lying quartet Fe^+ is populated, otherwise it might be made via a curve crossing from the sextet Fe^+ . While this is more than twice the bond energy we had previously calculated, this structure has tighter frequencies, and the upper limit of the effective second order rate constant is still many orders of magnitude smaller than the rate constant measured by the Bohme group.

We do agree with the statement from Bohme 2013 that it is unrealistic to assume $(\text{FeNO}^+)^*$ “needs to be stabilized to FeNO^+ before reacting further with NO”. However, this would only happen if the helium and NO concentrations were similar. However, it is unphysical to have the FeNO^+ excited state live for 1000’s of helium collisions; it will either fall apart or be stabilized. We note the claim in Bohme 2013 that experimental data has been well-fit through modeling of (5)-(6). In our own modeling, we can only achieve such fits by assuming a unimolecular dissociation rate constant of FeNO^+ of $\sim 10^2 \text{ s}^{-1}$ at threshold, many orders of magnitude smaller than for such a weakly bound triatomic species.³

Bohme 2013 argues the plausibility of (5)-(6) by citing analogous reactions reported by their group involving NO_2 and O_2 .^{4,5} Our argument against the three-body mechanism for $\text{Fe}^+ + \text{NO}$ is based on the time scale of the reaction specific to that system, depending on the vibrational and rotational frequencies and, significantly, on the dissociation energy of the complex. $\text{Os}^+ - \text{O}_2$ is bound by $\sim 5 \text{ eV}$,⁶ which is a value given in our original paper that would make $\text{Fe}^+ - \text{NO}$ stable enough for the termolecular mechanism to proceed. Indeed, stable OsO_2^+ is observed.⁴ $(\text{Metal-NO}_2)^+$ complexes are characterized by more low energy modes than those for

(Metal-NO)⁺ ones and may be more stable. Both effects result in an upper limit on the three-body mechanism that is several orders of magnitude higher than that for the termolecular NO mechanism. Therefore, these potential analogs do not apply directly to the (Fe-NO)⁺ system.

Impurity Analyses

Bohme 2013 focusses on monitor reactions with Hg⁺, Ge⁺, and As⁺.¹ The monitor reactions with Hg⁺ are confused by inconsistencies in the Bohme group's published reports. In the original paper on NO₂ reactivity with Hg⁺,⁵ Figure 2 shows NO⁺ as the dominant product, Table 1 lists NO₂⁺ as 98%, the discussion states “NO⁺ formation is the major channel”, and the conclusions state NO₂⁺ is the only product. In Bohme 2013 a mass spectrum at unspecified conditions shows that NO₂⁺ is the primary product formed from reaction with NO₂. Assuming then that NO₂⁺ is indeed the major product, there is still an issue with the test. In studying NO reactions without an NO₂ trap, which we postulate is 98-99% NO and 1-2% NO₂, one must consider that NO₂⁺ converts to NO⁺ rapidly by reaction 1 in our comment. As shown in figure S1, the NO₂⁺ signal would peak at only a few counts s⁻¹, near the threshold for detection, and only over a narrow range of low reactant flows. The ability to readily identify signals this small is twice contradicted in Bohme 2013 for similar systems: in the caption to Figure 1 “*The deviation of the FeO⁺ profile from linear behavior at low signal intensities (<30 counts s⁻¹) is attributed to the background*”; in the caption to Figure 3 “*The deviations of the As⁺ and AsO⁺ profiles from linear behavior at low signal intensities (<20 counts s⁻¹) are attributed to background*”. Thus, failure to observe <10 counts s⁻¹ NO₂⁺, which is less than the background signal (S/N <0.5), is not conclusive proof that NO₂ is absent.

Bohme 2013 also claims Ge⁺ was observed to produce NO₂⁺ in second order chemistry with NO₂, first producing GeO⁺. No NO₂⁺ was observed in the reaction of Ge⁺ with NO, which the authors specifically note was completed using the same physical gas mixture as used for the Fe⁺ experiments. The lack of observed second order chemistry for a 1-2% impurity that can then charge transfer to NO⁺ is hardly surprising, and by no means conclusive. Indeed, the peak NO₂⁺ signal expected from this reaction is even lower than that for Hg⁺ (Figure S1). Additionally, in their recent 2012 report on atomic cation reactions with NO₂,⁵ the Bohme group states that no higher order products were observed for Ge⁺, in contradiction to their statement in Bohme 2013.

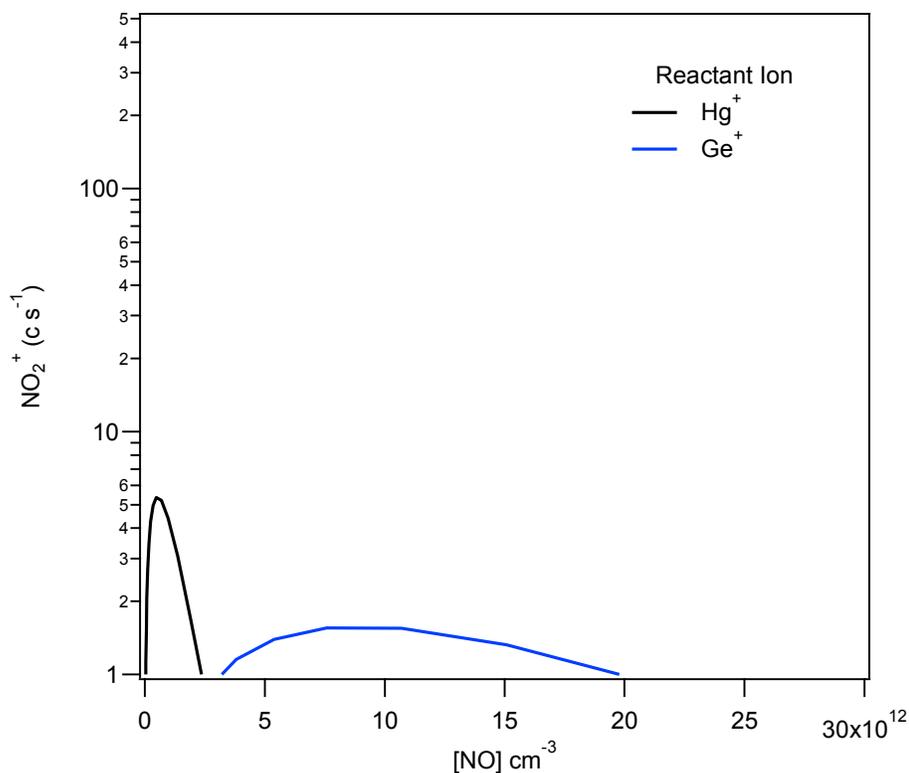


Figure S1. Modeled count rates of NO_2^+ expected from reaction of 500 initial c s^{-1} Hg^+ or Ge^+ with NO , assuming a 1.5% NO_2 impurity under conditions typically employed by the Bohme group. The Ge^+ chemistry assumes no termolecular reaction with NO ; including that reaction approximately doubles the NO_2^+ count rate at all reactant flows.

The monitor reaction with As^+ is also inconclusive. Bohme 2013 Fig. 3 shows raw data plots for the reactions of As^+ with both NO and NO_2 .¹ They conclude that because AsO^+ is the main product for the NO_2 reaction (and AsO^+ does not react with NO), a small amount of AsO^+ observed in the NO reaction should increase with NO flow if an NO_2 impurity is present. Because AsO^+ decreases slowly with NO flow, they conclude there is no NO_2 contaminant. Figure S2 shows their raw data, which we have digitized and fit by modeling with a 1.5% NO_2 impurity using rate constants published by the Bohme group.^{5,7,8} The modeling shows that a rise in the AsO^+ signal due to NO_2 impurity is small, and not easily detectable above the noise in the data. The shaded section in Figure S2 denotes where deviations are expected due to background, which includes the five highest flow points in the As^+ decline, and almost the entirety of the AsO^+ data. We note that our modeling fits the first ~15 data points of the As^+ and AsO^+ signals rather well, at the expense of missing the five data points at high flow (where the scatter is highest); the fit by the Bohme group to the As^+ decline shown in Bohme 2013 also emphasizes this point. Two brief asides warrant mentioning, the first being that the data presented in Bohme 2013 for $\text{As}^+ + \text{NO}$ appears identical to data they previously published; however both the x-axis

and y-axis are much different than previously published, such that the rates cannot be the same.^{1,9} Second, the explanation for the origin of AsO^+ stated in Bohme 2013 as due to water impurity is likely to be incorrect. The Bohme group has reported that As^+ reacts slowly with D_2O and produces AsO^+ in only 10% of reactions.¹⁰ Therefore, the observed AsO^+ signal requires a water impurity on the order of one part per thousand. A much more likely scenario is an O_2 impurity, which only needs to be present at one ppm to produce the observed AsO^+ .⁸

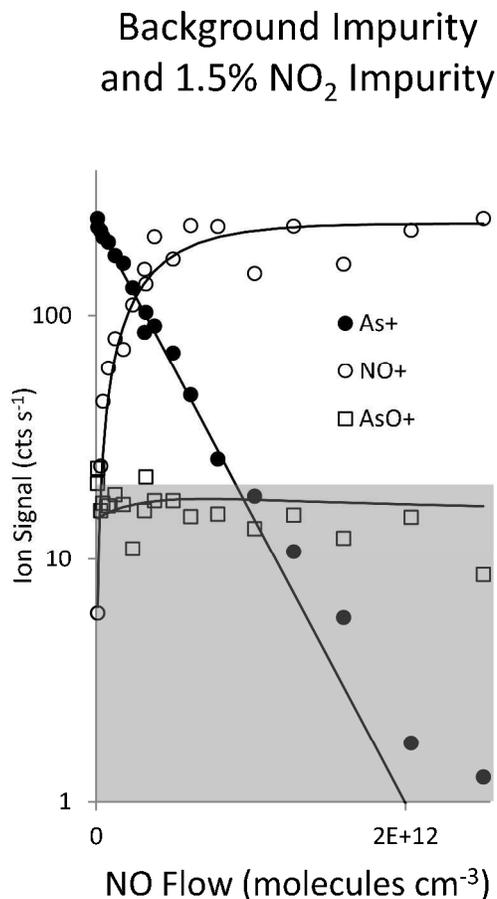


Figure S2. Our kinetic fits to data of the Bohme group for the reaction of $\text{As}^+ + \text{NO}$. We employ rate constants published by the Bohme group for all pertinent reactions. All fits assume a 1.5% NO_2 impurity. The shaded region represents the area where the Bohme group states “deviations...are due to background”.¹

While not discussed in Bohme 2013, both the 2005 and 2006 papers on NO reactivity^{7,11} cite the use of monitor reactions of ScO^+ , ZrO^+ , and LaO^+ , which produce NO^+ from reaction with NO_2 but not NO. The citation given for this, however, contains no data on these reactions.

We have been unable to find data on the reactions with ScO^+ or ZrO^+ , while the Bohme group's 2010 paper on NO_2 reactions of atomic lanthanide cations¹² lists the products of LaO^+ with NO_2 as LaO_2^+ and $\text{LaO}(\text{NO}_2)^+$, not NO^+ , in contradiction with the claim that LaO^+ produces NO^+ .

Experimental Details

Bohme 2013 questions whether differences in the gas handling systems between our two groups led to NO_2 impurities in our system, but not theirs. Due to the toxic nature of these gases, we were careful to leak check the entirety of the gas handling manifold. No Teflon parts were used. All lines, traps, and valves that are used up to and after the MKS flow meter for handling reagent gases and helium are stainless steel. Pumping lines are $\frac{1}{4}$ " stainless steel for approximately 3 feet and 1" stainless steel for an additional 5 feet up to PVC junctions to oil-free pumps.

In any case, the Ascarite trap results seem definitive. In those experiments, we see no reactivity with the trap in place. We then remove the trap, join the two stainless steel lines, and suddenly $\text{Fe}^+ + \text{NO}$ appears to react at a rate constant very similar to that reported by the Bohme group. While we could envision that in the process of removing the trap we introduce impurities, we reiterate: that situation leads to the perceived rate constants reported by Bohme and not a higher value. Replacing the trap and baking then reduces the rate constant by a factor of about 17, with all perceived reactivity ($1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$) attributed to a small N_2O impurity. Further testing with the Ascarite trap over time, with and without baking, and studying monitor reactions all confirm that $\text{Fe}^+ + \text{NO}$ does not react, as detailed in our previous publication.² In addition, the monitor reactions confirm that the trap is not removing the NO . From decades of experience with nitrogen oxides, we have learned the importance of trapping techniques when the chemistry is slow or for minor products – the case here. This in agreement with many others whom deal with nitrogen oxides.¹³⁻²¹ It would be a direct test of our hypothesis for the Bohme group to employ a baked Ascarite trap, or other suitable trap, and repeat their measurements.

NO Dimer

Although in all previous publications the Bohme group discounts the presence of the NO dimer (and we agree), they speculate that perhaps the dimer accounts for their observed reactivity, and is removed by our Ascarite trap. An argument against this is to assume a similar dissociation behavior for NO dimer as that of other nitrogen oxides. The first order rate constants for dissociations of N_2O_3 , N_2O_4 , and N_2O_5 are all well established and approximately equal to $(10^{15} \text{ to } 10^{16}) \times \exp(-E_{\text{dis}}/RT) \text{ s}^{-1}$, where E_{dis} is the dissociation energy, R is the gas constant, and T is the temperature. The dissociation energy of the NO dimer is on the order of 2.0 kcal mol⁻¹

^{1, 22, 23} which yields a room temperature dissociative lifetime below 10^{-12} s, far too small for NO dimer to contribute to reactivity under the experimental conditions (10^{-2} s).

Branching Ratio Analysis

Figure 1 of Bohme 2013 argues that no (or very little) NO^+ is formed from the primary reaction of $\text{Fe}^+ + \text{NO}_2$; we contend that their data is best described by an approximately 20% branching due to reaction of $\text{Fe}^{+*} + \text{NO}_2$. The fits to the right hand side of their figure, from which branching fractions are derived, do not appear consistent with those on the left hand side; note the left hand side fits underestimate NO^+ at low flow while fitting FeO^+ , while the right hand side fits pass through all data points. Our understanding is that the left hand side fits are from kinetic modeling, while the right hand side fits are simply an exponential or double exponential fit (private communication) of the form

$$A * e^{-B[\text{NO}_2]} + C * e^{-D[\text{NO}_2]}$$

That solution does not represent the true kinetics derived through full kinetic modeling of the system. For this case, with the reaction scheme



an analytical solution is available:

$$[\text{Fe}^+]_t = [\text{Fe}^+]_0 e^{-k_1 t [\text{NO}_2]}$$

$$[\text{FeO}^+]_t = [\text{Fe}^+]_0 \left(\frac{k_{1a}}{k_2 - k_1} e^{-k_1 t [\text{NO}_2]} + \frac{k_{1a}}{k_1 - k_2} e^{-k_2 t [\text{NO}_2]} \right)$$

$$[\text{NO}]_t = [\text{NO}]_{t,(1b)} + [\text{NO}]_{t,(2)}$$

$$[\text{NO}^+]_{t,(1b)} = [\text{Fe}^+]_0 \frac{k_{1b}}{k_1} (1 - e^{-k_1 t [\text{NO}_2]})$$

$$[\text{NO}^+]_{t,(2)} = [\text{Fe}^+]_0 \left(-\frac{k_{1a} k_2}{(k_2 - k_1) k_1} e^{-k_1 t [\text{NO}_2]} - \frac{k_{1a}}{(k_1 - k_2)} e^{-k_2 t [\text{NO}_2]} + \frac{k_{1a} k_2}{k_1 k_2} \right)$$

Figure S3 displays three attempts to fit the data with these equations. The top panel reproduces the exponential fit from Bohme 2013 well by assuming a collisional primary rate ($k_{\text{coll}}=8.9 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$; essentially their measured value) and primary branching to NO^+ of <5%. However, this good fit requires a secondary rate constant $k_2=1.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. This value is problematic, both because k_2 is supercollisional outside of error ($k_{\text{coll}}=8.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$) and data from both our lab and the Bohme group agree that k_1 and k_2 must be within 10% of each other.^{2,24} Placing these

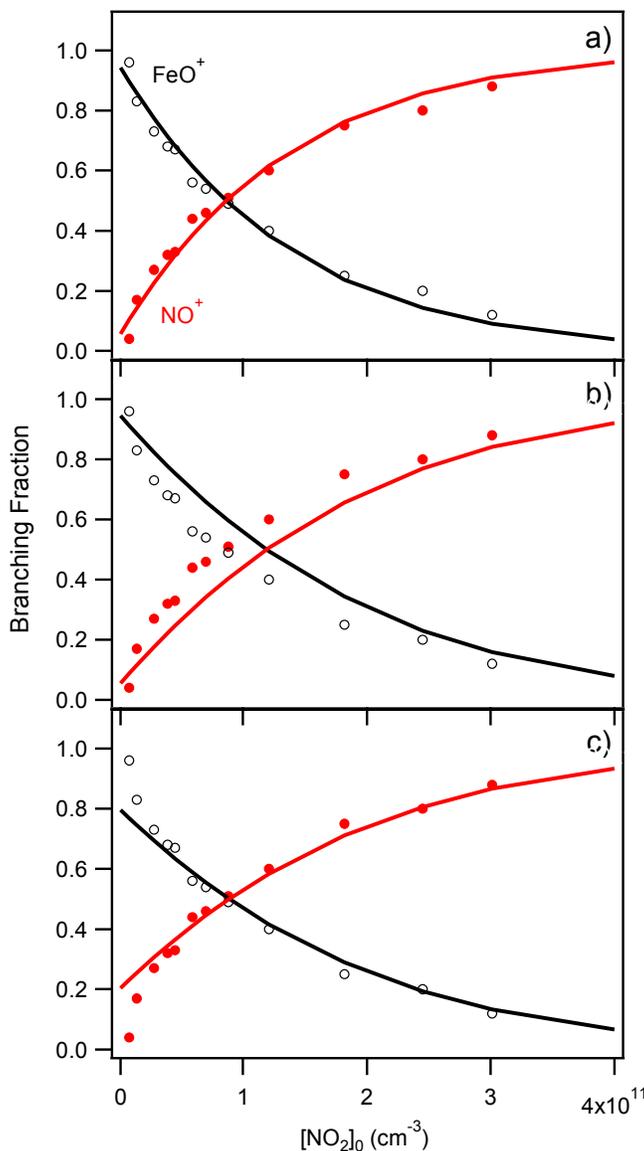


Figure S3. Analytical solution fits to the product branching data shown in Bohme 2013 Fig. 1.¹ a) Unphysical fit required to reproduce the exponential fit reported in Bohme 2013 ($k_{1a}=8.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$; $k_{1b}=5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$; $k_2=1.4 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$) b) Best fit restricting k_2 to within 10% of the collisional value and NO^+ primary branching to <0.05 ($k_{1a}=8.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$; $k_{1b}=5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$;

$k_2=1.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$) c) Best fit restricting k_2 to within 10% of the collisional rate ($k_{1a}=7.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$; $k_{1b}=1.8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$; $k_2=1.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$), with branching to NO^+ of ~20%.

restrictions on the rate constants, we are unable to fit the full data set. For the middle panel, k_1 is again taken as the collision rate and k_2 is restricted to be within 10% of the collisional value while maintaining a primary branching to NO^+ of <5%. The data are poorly fit over almost the entire range. Note that reducing the rate constants produces worse fits and raising the rate constants makes them supercollisional, so that is the best one can do. Finally, the lower panel keeps both rates within 10% of each other and the collision rate, while allowing the branching ratio to vary freely. The fit shown (20% branching) fits most of the data but not the lowest flow points for which the Bohme group has conceded have larger concentration errors. Interpretation of the data is then not clear cut. We believe that 20% branching is the best available explanation, and is most consistent with other available data as explained in our original publication.² In that paper, we give a detailed analysis based on modeling the full chemistry of the system with a Monte Carlo sampling of all possible rate constants and arrive at the same conclusion as that presented here. While in many cases product branching ratios may be derived using a simplified treatment, that is not the case here. The exponential fits shown in Bohme 2013 Figure 1 as definitive evidence of small primary NO^+ branching do not have a physical basis for this reaction scheme, and the actual kinetic solution should be used.

References

- (1) Blagojevic, V.; Jarvis, M. J. Y.; Koyanagi, G. K.; Bohme, D. K. Role of $(\text{NO})_2$ Dimer in Reactions of Fe^+ with NO and NO_2 Studied by ICP-SIFT Mass Spectrometry. *J. Phys. Chem. A* **2013**, *117*, 3786-3790.
- (2) Melko, J. J.; Ard, S. G.; Fournier, J. A.; Shuman, N. S.; Troe, J.; Viggiano, A. A. Exploring the Reactions of Fe^+ and FeO^+ with NO and NO_2 . *J. Phys. Chem. A* **2012**, *116*, 11500-11508.
- (3) Baer, T.; Hase, W. L. *Unimolecular Reaction Dynamics: Theory and Experiments*; Oxford University Press: Oxford, 1996.
- (4) Koyanagi, G. K.; Caraiman, D.; Blagojevic, V.; Bohme, D. K. Gas-phase Reactions of Transition-metal Ions with Molecular Oxygen: Room-temperature Kinetics and Periodicities in Reactivity. *J. Phys. Chem. A* **2002**, *106*, 4581-4590.
- (5) Jarvis, M. J. Y.; Blagojevic, V.; Koyanagi, G. K.; Bohme, D. K. Nitrogen Dioxide Reactions with 46 Atomic Main-Group and Transition Metal Cations in the Gas phase: Room Temperature Kinetics and Periodicities in Reactivity. *J. Phys. Chem. A* **2012**, *117*, 1151-1157.
- (6) Hinton, C. S.; Citir, M.; Armentrout, P. B. *Int. J. Mass Spectrom. Ion Processes* **2013**, *In Press*.
- (7) Blagojevic, V.; Flaim, E.; Jarvis, M. J. Y.; Koyanagi, G. K.; Bohme, D. K. Nitric Oxide as an Electron Donor, an Atom Donor, an Atom Acceptor, and a Ligand in Reactions with Atomic Transition-Metal and Main-Group Cations in the Gas Phase. *J. Phys. Chem. A* **2005**, *109*, 11224-11235.
- (8) Bohme, D. K. *Ion Chemistry Laboratory Centre for Research in Mass Spectrometry*; York University: Toronto, ON; <http://www.chem.yorku.ca/profs/bohme/research/molecule/O2.html> (retrieved May 2, 2013)

- (9) Jarvis, M. J. Y.; Blagojevic, V.; Koyanagi, G. K.; Bohme, D. K. Energy Resonance in Electron Transfer from Nitric Oxide to Atomic Metal Cations at Room Temperature. *Chem. Phys. Lett.* **2005**, *416*, 268-271.
- (10) Cheng, P.; Koyanagi, G. K.; Bohme, D. K. Heavy Water Reactions with Atomic Transition-Metal and Main-Group Cations: Gas Phase Room-Temperature Kinetics and Periodicities in Reactivity. *J. Phys. Chem. A* **2007**, *111*, 8561-8573.
- (11) Blagojevic, V.; Flaim, E.; Jarvis, M. J. Y.; Koyanagi, G. K.; Bohme, D. K. Gas-phase Reactions of Nitric Oxide with Atomic Lanthanide Cations: Room-temperature Kinetics and Periodicity in Reactivity. *Int. J. Mass Spectrom.* **2006**, *249–250*, 385-391.
- (12) Jarvis, M. J. Y.; Blagojevic, V.; Koyanagi, G. K.; Bohme, D. K. Nitrogen Dioxide Reactions with Atomic Lanthanide Cations and Their Monoxides: Gas-phase Kinetics at Room Temperature. *Phys. Chem. Chem. Phys.* **2010**, *12*, 4852-4862.
- (13) Poth, L.; Shi, Z.; Zhong, Q.; Castleman Jr, A. W. Study of the Reaction of NO Clusters with Water Using a Pickup Technique. *Int. J. Mass Spectrom. Ion Processes* **1996**, *154*, 35-42.
- (14) Rawlins, W. T.; Foutter, R. R.; Parker, T. E. Vibrational Band Strengths and Temperatures of Nitric Oxide by Time-resolved Infrared Emission Spectroscopy in a Shock Tube. *J. Quant. Spectrosc. Radiat. Transfer* **1993**, *49*, 423-431.
- (15) Wanat, A.; Schnepf, T.; Stochel, G.; van Eldik, R.; Bill, E.; Wiegardt, K. Kinetics, Mechanism, and Spectroscopy of the Reversible Binding of Nitric Oxide to Aqueous Iron(II). An Undergraduate Text Book Reaction Revisited. *Inorg. Chem.* **2001**, *41*, 4-10.
- (16) Ray, G. W.; Watson, R. T. Kinetics of the Reaction Nitric Oxide + Ozone → Nitrogen Dioxide + Oxygen from 212 to 422 K. *J. Phys. Chem.* **1981**, *85*, 1673-1676.
- (17) Piper, L. G.; Rawlins, W. T. Oxygen-atom Yields from Microwave Discharges in Nitrous Oxide/Argon Mixtures. *J. Phys. Chem.* **1986**, *90*, 320-325.
- (18) Morris, R. A.; Viggiano, A. A. Chemistry of PO^- , PO_2^- , and PO_3^- in the Gas Phase. *J. Chem. Phys.* **1998**, *109*, 4126-4127.
- (19) Van Doren, J. M.; Viggiano, A. A.; Morris, R. A.; Miller, A. E. S.; Miller, T. M.; Paulson, J. F.; Deakynne, C. A.; Michels, H. H.; Montgomery, J. A., Jr. Experimental and Theoretical Study of the Reaction of HO^- with NO. *J. Chem. Phys.* **1993**, *98*, 7940-7950.
- (20) Poth, L.; Shi, Z.; Zhong, Q.; Castleman, A. W. Metastable Dissociation Study of Nitric Oxide Clusters. *J. Phys. Chem. A* **1997**, *101*, 1099-1103.
- (21) Lim, M. D.; Lorkovic, I. M.; Ford, P. C. In *Nitric Oxide, Pt E*; Packer, L., Cadenas, E., Eds. 2005; Vol. 396, p 3-17.
- (22) Potter, A. B.; Dribinski, V.; Demyanenko, A. V.; Reisler, H. Exit Channel Dynamics in the Ultraviolet Photodissociation of the NO Dimer: $(\text{NO})_2 \rightarrow \text{NO}(\text{A}^2\Sigma^+) + \text{NO}(\text{X}^2\Pi)$. *J. Chem. Phys.* **2003**, *119*, 7197-7205.
- (23) Wade, E. A.; Cline, J. I.; Lorenz, K. T.; Hayden, C.; Chandler, D. W. Direct Measurement of the Binding Energy of the NO Dimer. *J. Chem. Phys.* **2002**, *116*, 4755-4757.
- (24) Baranov, V.; Javahery, G.; Hopkinson, A. C.; Bohme, D. K. Intrinsic Coordination Properties of Iron in FeO^+ : Kinetics at 294+/-3 K for Gas-phase Reactions of the Ground States of Fe^+ and FeO^+ with Inorganic Ligands Containing Hydrogen, Nitrogen, and Oxygen. *J. Am. Chem. Soc.* **1995**, *117*, 12801-12809.