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pected that charge transfer is more likely the longer the duration of the collision.

It is possible that a detailed reaction theory could predict the temperature dependence quantitatively for one or more statistical models and thus bear on unimolecular decomposition theory in a new manner.

[1] D. B. Dunkin, F. C. Fehsenfeld, A. L. Schmeltekopf, and E. E. Ferguson, J. Chem. Phys. **49**, 1365 (1968).

[2] C. F. Giese, Advan. Chem. Ser. **58**, 20 (1966).

[3] R. F. Stebbings, J. A. Rutherford, and B. R. Turner, J. Geophys. Res. **71**, 771 (1966).

[4] D. K. Bohme, D. B. Dunkin, F. C. Fehsenfeld, and E. E. Ferguson, J. Chem. Phys. **49**, 5201 (1968). Also E. E. Ferguson, D. B. Dunkin, F. C. Fehsenfeld, and A. L. Schmeltekopf, Bull. Am. Phys. Soc. **13**, 212 (1968).

[5] H. S. Johnston, *Gas Phase Reaction Rate Theory* (Ronald Press Co., New York, 1966), Chap. 15.

[6] J. C. Light, J. Chem. Phys. **40**, 3221 (1964); P. Pechukas and J. C. Light, *ibid.* **42**, 3281 (1965).

Interpretation of Nuclear Quadrupole Constants in Compounds of 181Ta

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Recently some nuclear quadrupole constants in compounds of 181Ta of low oxidation states have been measured[1-3] by several groups studying the perturbed angular correlation in the cascade $(\frac{1}{2})$ 133 keV $(\frac{5}{2})$ 482 keV $(\frac{7}{2})$, where the intermediate state has a lifetime $\tau_N = 15.8$ nsec. The compounds used were HfO_2, $HfOCl_2 \cdot 8H_2O$, and Hf metal. From the known nuclear quadrupole moment (Q) of 181Ta [using the formula $|V_{zz}| = 2I(2I+1)\hbar\omega_0/3eQ$] electric field gradients (efg) produced by the atomic or molecular environment of the decaying nucleus were derived.

In this Note we have interpreted these electric field gradients in terms of the ligand–field theory[4] which is mainly concerned with the effect of electrostatic potentials of different symmetries on electronic wavefunctions. Neglecting effects of hybridization, we can write a theoretical expression for the efg:

$$V_{zz} = \sum_{nlm} |a_{nlm}|^2 q_{nlm,nlm},$$

where

$$q_{nlm,nlm} = -e(\tfrac{16}{5})^{1/2} \int \psi_{nlm} Y_2^0 \psi_{nlm}* dz$$

are the values of the efg for each atomic state. The ψ_{nlm}'s are the wavefunctions of the ground state of the electronic configuration.

The nucleus 181Ta originates from the decay of 181Hf; we shall assume that the electronic rearrangement following the decay occurs sufficiently fast so as to ensure that the experimentally measured quadrupole constants refer to the Ta compound structure.

From atomic spectroscopy, we known that the ground term for 181Ta is $^4F_{3/2}$ and the configuration of the outer electrons is $(5d^3)(6s^2)$. As closed orbits and s wavefunctions do not contribute to the efg we need only to take into account the terms with $n=5$, $l=2$, in the given expression.

The electronic wavefunctions for a single $5d$ electron and for three $5d$ electrons may be obtained from Ref. 5, and following Ref. 4 one can find the effect of an electrostatic potential on ground terms ^4F for different local crystalline structures of the environment of the central atom(in our case, the atom of 181Ta). An electrostatic potential produced by ions forming an octahedron, a tetrahedron or a cube splits the energy levels for d functions. This splitting for electron configurations d^1 and d^3 is also given in Ref. 4. For d^1, there is a splitting in two orbital sets $d\epsilon$ (threefold orbitally degenerate) and $d\gamma$ (twofold orbitally degenerate). For d^3, there is a splitting in three orbital sets T_1 (threefold orbitally degenerate), T_2 (threefold orbitally degenerate), and A_2 (not orbitally degenerate). Distortions of cubic symmetries are treated as perturbations. Their main effect is to lift the orbital degeneracy, leaving an electronic ground state.

With this theoretical background, it is possible to analyze the efg given in Table I:

(a) The crystalline structure of TaO_2 has cubic symmetry[6] and its electron configuration is d^1. A cubic symmetry leaves a doubly degenerate ground term E but a tetragonal distortion lifts the orbital degeneracy, resulting[4] in a ground state $|x^2-y^2\rangle$.

(b) The local crystalline structure of Ta in $HfOCl_2 \cdot 8H_2O$ has tetragonal symmetry.[6] Its electron configura-

TABLE I. Comparison between experimental derived and theoretical estimated electric field gradients.

Compound	Electron configuration for Ta	Ground wavefunctions	q in units $\langle r^{-3} \rangle_{n=5}$	$\|V_{zz}\|$ 10^{17} V/cm³	Reference
Hf metal	d^3	$\langle 0 \rangle$	$\frac{2}{5}(4/7)$	5.2 ± 0.3	1
HfO_2	d^1	$|x^2-y^2\rangle$	$4/7$	13.5 ± 1.2	2
$HfOCl_2 \cdot 8H_2O$	d^1	$|x^2-y^2\rangle$	$4/7$	13.3 ± 1.2	3

tion is also d^1. It follows that we can assume for the ground state the form $| x^2 - y^2 \rangle$.

(c) The crystalline structure of metallic Ta is of cubic symmetry (bcc). Its electron configuration is d^3. The effect of an electrostatic potential due to a cubic charge distribution is to split the energy level leaving T_1 as the ground state. A tetragonal distortion lifts this threefold orbital degeneracy resulting[4] in a ground state $\langle 0 \rangle$.

Based on these assumptions, the values for q_{nlm} in units of $\langle r^{-3} \rangle_{n=5}$ were calculated and are given in Table I.

The ratios of the theoretical values of q_{nlm} show good agreement with the ratios of the experimental values of V_{zz} in compounds of the same and of different oxidation states. This fact indicates that the effects of perturbing distortions on cubic symmetries are mainly responsible for the efg produced at the nucleus in chemical compounds of low oxidation states and that in these cases the ligand–field theory can be applied. The comparison also tells us that the efg acting on ^{181}Ta in these compounds are positive.

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[1] R. W. Sommerfeldt, T. W. Cannon, L. W. Coleman, and L. Schecter, Phys. Rev. **138**, B763 (1965).
[2] G. Marest, I. Berkes, G. Bougnot, and R. Bernard, Compt. Rend. **262**, B367 (1966).
[3] P. da R. Andrade, A. Maciel, and J. D. Rogers, Phys. Rev. **159**, 196 (1967).
[4] B. N. Figgis, *Introduction to Ligand Field Theory* (Interscience Publishers, Inc., New York, 1966).
[5] J. E. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Co., New York, 1960), Vol. 2.
[6] F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry* (Interscience Publishers, Inc., New York, 1966).

Observation of Charge Exchange in Xenon–Methane Mixtures by Ion-Cyclotron Double Resonance*

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One of the intriguing results in the literature of ion–molecule reactions has been the failure of Field and Franklin to observe charge exchange in a xenon–methane mixture at elevated pressure in a mass-spectrometer ion source.[1] The ionization potential of methane has been determined recently in a photoionization study to be about 12.6 eV,[2] while the recombination energies of the $^2P_{3/2}$ and $^2P_{1/2}$ states of Xe$^+$ are 12.13 and 13.44

eV,[3] respectively. Thus charge exchange of the $^2P_{1/2}$ state with CH_4 to produce the methane molecular ion is clearly exothermic. Furthermore, this reaction has been observed in tandem mass-spectrometer experiments using accelerated and mass-selected Xe$^+$ [4–7] and in single-source mass-spectrometer experiments using pulse methods[7,8] or other techniques[9,10] to perturb the normal steady-state distribution of ions.

To explain their unexpected results Field and Franklin suggested that either charge exchange did not occur between thermal velocity Xe$^+$ and methane molecules or that no net charge exchange occurs, the charge exchange between Xe$^+$($^2P_{1/2}$) and methane being exactly balanced by charge exchange of CH_4^+ with xenon to produce Xe$^+$($^2P_{3/2}$). The recombination energies of relaxed CH_4^+ range from 9 to 12 eV,[11] so the latter explanation is plausible. Using ion-cyclotron double resonance,[12] King and Elleman recently presented evidence that this balance of reactions occurs.[13] Their results also indicated that the charge-exchange reaction between CH_3^+ and Xe occurs, although it must be endothermic by 2.29 eV for ground-state ions[3,14] and by at least 1.5 eV for the distribution of ion energies formed by electron impact.[11]

For several months we have been studying ion–molecule reactions by ion-cyclotron resonance techniques for several systems whose reactions have been well characterized by established techniques. In most cases there has been at least qualitative agreement with earlier results, but in a few cases we have found clearcut contradictions. These appear to be attributable to two artifacts in ion-cyclotron resonance experiments, the extreme sensitivity to space charge (because of ion trapping in the strong magnetic field for low-energy ions) and ill-defined ion losses with low and moderate irradiating fields (i.e., "leakiness" of the ICR cell because actual electrostatic fields deviate substantially from the idealized fields assumed in calculations). It occurred to us that these phenomena may have been involved in the charge exchange study, and we have reinvestigated the xenon–methane system.

In our experiments a 3:1 mixture of methane and xenon was investigated by ion-cyclotron resonance using various irradiation schemes. The results are displayed in Fig. 1. Figures 1(a) and 1(b) are double-resonance spectra[12] in which CH_4^+ is observed while the irradiating oscillator is swept over the Xe$^+$ resonance region, and ^{129}Xe$^+$ is observed while the irradiating oscillator is swept over the resonance frequencies of CH_3^+ and CH_4^+, respectively. Figure 1(b) is substantially equivalent to King and Elleman's Fig. 1.[13]

Because ion-cyclotron resonance peaks are so sharp in a properly tuned system, and because a shift in space charge (as by irradiating ions out of the cavity in a double-resonance experiment) can shift the resonant frequency by a few gauss, erroneous signals are sometimes generated. Accordingly, we find it desirable