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The abscissa in Fig. 3 of Ref. 1 is in error and the plot should be replaced by the equivalent figure below. As before, the experimental rate constants $k_{X+YY}$ refer to the formation of the isotopologues $XYY$ of ozone, where $X$ and $Y$ denote any of the three isotopes $^{16}O$, $^{17}O$ and $^{18}O$. The masses of $X$ and $Y$ in the figure are denoted by $m_X$ and $m_Y$, respectively.

The plot illustrates, as before, the empirical correlation of experimentally measured rate constant ratios with a ratio of masses, there being many different abscissas which show the correlation, all being functionally related. As noted in Ref. 1, different forms of the abscissa include ratios of diatomic moments of inertia and differences in diatomic zero-point energies. Compare also the correlation with the latter difference in Ref. 4 and with the analogous enthalpy difference in Ref. 5.

The conclusion is identical with that drawn in Ref. 1, namely that a correlation alone does not establish the origin of the differences in the experimental rate constant ratios $k_{X+YY}/k_{o+66}$. In the terminology of transition state theory the origin, first established by Gao and Marcus, is due to the difference in partitioning factors in the two exit channels of the dissociation of the vibrationally excited intermediate $XYY^*$, which in turn is due to the difference in zero-point energy in the two exit transition states (TS). The latter TS are almost “loose” and so the differences are then those of the diatomic molecules in those two TSs. The “quantum states” in the transition state serve as approximate doorway states to the Feshbach resonant states of the vibrationally excited molecule $XYY^*$ formed in the recombination step, and so the effect discussed above can be described in the fundamental language of scattering theory.

As before, the three points where $X=Y$ are not included in the figure. They form symmetric vibrationally excited ozone molecules $XXX^*$, some of whose anharmonic vibrational-vibrational and rotational-vibrational intramolecular couplings responsible for “RRKM” behavior are forbidden by symmetry restrictions. These $X+XX$ points are approximately 15% below the line in the figure. These three points show the drawback of a purely empirical correlation. Why they are not on the line is understood in terms of the theory in Refs. 6–8.

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FIG. 1. Plot of ratio of experimental rate constants (Ref. 3) versus ratio of masses in the formation of $XYY$ from $X+YY$. The straight line is intended only as a guide to the eye.
2I am very much indebted to Dr. Reinhard Schinke for calling my attention to this error.