

Does Symmetry Drive Isotopic Anomalies in Ozone Isotopomer Formation?

Gao and Marcus (1) presented a modified Rice, Ramsperger, Kassel, Marcus (RRKM)-based theory to explain the strange and unconventional ozone isotope effect that has puzzled scientists for years. In earlier studies, mass spectrometric (2, 3) and diode laser (4) measurements of ozone isotopomers in "scrambled" oxygen mixtures pointed toward a symmetry origin for isotope fractionation. Kinetic studies, however, contradicted the dominant role of symmetry (5, 6), and later experiments revealed an unconventional mass dependency, in which isotopomer formation correlates with the enthalpy of the competing isotopic exchange (7). Marcus and co-workers (1, 8) have offered a solution to this puzzle by imposing two different fractionation factors. The first was incorporated into the theory as an ad hoc factor to describe possible nonstatistical effects, which affect asymmetric and symmetric molecule formation differently. The second, which can be called zero-point energy fractionation (ZPEF), can be treated within the RRKM theory and relates to competing properties of the exit channel transition states (1, 8).

Although the theory of Gao and Marcus successfully explains most of the experimental data (3–7), their conclusion that "the key isotope effects . . . are in a sense symmetry-driven" is likely to be misunderstood. Of course the ad hoc factor, which has been determined by a fit to the experimental data in (3), is of a pure symmetry origin, and in this context the term "symmetry-driven" is clearly appropriate. The same term should be avoided to describe ZPEF, however, because this kind of fractionation is connected only accidentally, not causally, with molecular symmetry.

The experimental data show a linear correlation between asymmetric molecule formation and the enthalpy of the competing isotopic exchange. Symmetric molecules also fit into this scheme when other contributions are corrected for (9). In the modified RRKM theory (1, 8), ZPEF arises from so-called partitioning factors, which can be interpreted as microcanonical branching ratios for a vibrationally excited ozone molecule, XYZ*, to dissociate into either of two channels, XY + Z or X + YZ. These ratios certainly depend on atomic masses (through the number of states leading to either dissociation), but there is no dependence on molecular symmetry. At the same time, it immediately follows from this unusual mass dependence

that symmetric molecules are all formed at about the same rate. Thus, ZPEF bears a relation to symmetry, but is not a consequence of it.

Readers of the Gao and Marcus research article looking for a concluding explanation might not be aware of the noncausal connection between ZPEF and symmetry for two reasons: (i) Little can be learned about the physics behind this fractionation when the statement is interpreted to the effect that no causal connection exists. (ii) In a single statement in the article, both "key isotope effects" are referred to as symmetry-driven, even though only one of them is fundamentally connected with symmetry. The accompanying Perspective (10) apparently confirms that this fundamental difference between the two effects can easily be overlooked: According to that commentary, in the Gao and Marcus model, "there is no mass dependency but rather a subtle symmetry factor that produces the anomalous ozone" (10)—clearly an incorrect description of the underlying physics.

The ozone isotope effect shows two different and highly unusual fractionation factors not yet observed in any other chemical system. Although one of the "key isotope effects" identified by Gao and Marcus (1) is of quantum-mechanical symmetry origin, the other is only accidentally but by no means causally connected to molecular symmetry. Its origin has to be sought in differences of zero-point energies (7, 9) or other physical quantities that affect the competition between the transition states and also depend on atomic masses (1, 8).

Christof Janssen

Max-Planck-Institut für Kernphysik
Atmospheric Physics Division

Post Office Box 103980

69029 Heidelberg Germany

E-mail: christof.janssen@mpi-hd.mpg.de

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Response: Gao and I noted that the two key unconventional isotope effects in ozone formation "are in a sense symmetry-driven" (1). As Janssen observes, the relation to symmetry for one of these effects, a non-statistical behavior, is clear. The sense in which a second key factor is symmetry driven is more subtle (1–3): A large unconventional mass-dependent effect is observed under experimental conditions very different from those in which the "mass independent" behavior is seen. It arises from deviations of the partitioning factors Y_a and Y_b from the value of 1/2 (1, 2). The Y factors, determined from RRKM theory, are always 1/2 for the symmetric isotopomers and never 1/2 for asymmetric ozone isotopomers (1, 3). In this particular sense, the Y factor can be termed symmetry-driven. It could also be misunderstood, however, because unconventional isotope effects due to the Y factor can occur even when the dissociating molecule never has a symmetric isotopomer.

Janssen also discusses a correlation between different experimental variables. We have pointed out (4) that a correlation exists between the large mass-dependent isotope effects observed for ratios of rate constants and quantities such as ratios of reduced masses in exit channels, ratios of moments of inertia, and ratios related to differences of zero-point energies of the exit channels. We have shown that a correlation with one of these variables automatically implies a correlation with the other two, since all three quantities are functionally related (4). Thus, a correlation itself does not establish which of the three factors is its dominant cause. The calculations reveal that the small difference of zero-point energies is the primary factor (1, 3). Particularly surprising was the large effect of these small differences. It was shown to arise from the large difference in the number of accessible states in the transition state for each exit channel and, hence, in the values for Y_a and Y_b (1, 3). The number of accessible states for a given channel varies approximately as a quadratic power of the threshold energy of that channel, resulting in a large amplification of a small difference in threshold energies due to the small difference in zero-point energies (1, 3).

Finally, Janssen comments in passing on the Perspective by Thiemens (5) that accompanies our article. It should be noted that for the experiments of Thiemens, the Y

factors do not contribute—only the sum Y_a

Y_b appears, and it equals unity (2). Thus, in Thiemens's experiments, only the nonstatistical factor, which is clearly symmetry related, contributes. By contrast, the Y factors, not specifically discussed in (5), are dominant in (6). Thus, both the Thiemens type of experiment (5) and the recent series of Janssen *et al.* (6) are important and are seen to be complementary (1–4).

TECHNICAL COMMENTS

R. A. Marcus

Noyes Laboratory of Chemical Physics

Mail Code 127-72

California Institute of Technology

Pasadena CA 91125–7200 USA

E-mail: ram@caltech.edu

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