SPECIAL FEATURE: PERSPECTIVE

Theory of mass-independent fractionation of isotopes, phase space accessibility, and a role of isotopic symmetry

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Key experimental and theoretical features of mass-independent fractionation (MIF) of isotopes, also known as the η-effect, are summarized, including its difference from the exit channel zero-point energy difference effect. The latter exactly cancels in the MIF. One key experimental result is that the MIF for O_3 formation is a low-pressure phenomenon and, moreover, that it decreases with increasing pressure of third bodies at pressures far below the "Lindemann fall-off" pressures for three-body recombination of O and O_2. A possible origin of the MIF is discussed in terms of a role for isotopologue symmetry in intramolecular energy sharing. An explanation is suggested for the large difference in the fall-off pressure for recombination and the pressure for a large decrease in MIF, in terms of a difference between deactivating collisions and what we term here "symmetry-changing collisions". It is noted that the theory of the MIF involves four recombination rate constants and an equilibrium constant, for each trace isotope, seven rate constants in all and two equilibrium constants. A conceptual shortcut is noted. Experimental and computational information that may provide added insight into the MIF mechanism and tests is described.

anomalous pressure effect | ergodic | quasi-periodic | RRKM | chaperon

The discovery of the mass-independent fractionation (MIF) of isotopes in ozone formation by Thiemens and Heidenrich in the laboratory in 1983 (1, 2) is a well-recognized milestone in the study of isotope effects and a subject of papers in this journal issue [*cf.* also several reviews, refs. 3–6). In the present article, we note that there is also a very interesting zero-point energy difference (ΔZPE) effect (7) that is well understood in terms of RRKM (Rice-Ramsperger-Kassel-Marcus) theory (8–12). Instead, we focus on the MIF, considering it in terms of a deviation from statistical behavior. We recall that a factor η (the "η-effect") was introduced by Hathorn and Marcus (8, 9) and explored further by Gao and Marcus (10, 11) and Gao, Chen, and Marcus (12) to treat many aspects of the MIF. To consider a quantum dynamical origin of η, we discuss the intramolecular dynamics involved. In particular, we now incorporate the experimental result that the pressure effect on the MIF occurs at pressures far lower than those for the three-body deactivation in the recombination rate. A key question, which remains to be answered, is whether the symmetric isotopologues deviate from statistical behavior (non-RRKM) more than do the asymmetric isotopologues and whether, thereby, their lifetime is shorter and the corresponding rate of formation of the O_3 by deactivation of O_3^* is smaller. When ^{17}O and ^{18}O are present in only trace amounts, the only asymmetric ozone isotopologues are OOQ, where Q denotes ^{17}O as ^{18}O, whereas the symmetric isotopologues are OQO and OOO. The symmetric isotopologues OOO and OQO have half the density of vibrational rotational states due to symmetry restrictions, and we look at the consequences of that difference in terms of having fewer accidental resonances. Fewer accidental resonances mean less energy sharing and so less statistical behavior with a consequence of a shorter lifetime of O_3^* at low pressures, as discussed later.

In discussing vibrationally excited O_3 formed from $O + O_2$ and a possible physical basis for the η-effect we consider some concepts of the dynamics of anharmonic vibrational–rotational motion and in particular of regular (quasi-periodic) vs. chaotic classical mechanical behavior and its semiclassical and quantum counterparts (13–21). The analysis is conceptual rather than computational and is a prelude to a more detailed discussion elsewhere.

This article is intended to be, in part, an overview and, in part, to describe some unique ideas, including providing more detail on a suggested molecular basis for the postulated η-effect and a potential role for long-range symmetry-changing collisions.

Isotopic Enrichment

We first recall that the isotopic enrichment δ^Q of an isotope Q of oxygen in the formation of ozone is defined in mils (22, 23):

$$\frac{\delta^Q}{1000} = \frac{(\mathrm{Q/O})\text{ in ozone}}{(\mathrm{Q/O})\text{ in oxygen}} - 1. \qquad [1]$$

Eq. **1** can be rewritten in terms of the amounts of the molecular species as

$$\frac{{}^Q\delta}{1000} = \left[\frac{\mathrm{QOO + OQO}}{3\mathrm{O_3}} \Big/ \frac{\mathrm{QO}}{2\mathrm{O_2}}\right] - 1, \qquad [2]$$

where Q denotes ^{17}O or ^{18}O throughout. The expression for ${}^Q\delta$ in terms of the $O + O_2$ recombination rate constants is given by (8, 9)

$$\frac{{}^Q\delta}{1000} = 2\frac{k^s_{6,q6} + k^{s5}_{6,q6} + k^{as}_{q,66}K_{\mathrm{ex}}}{3k^5_{6,66}} - 1, \qquad [3]$$

where *s* denotes the isotopically symmetric isotopologue OQO and OOO and *as* is the asymmetric isotopologue OOQ. When formed from O and QO, it has a rate constant $k^a_{6,q6}$ and when formed from Q and OO, it has a

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rate constant $k^{s}_{q,66}$. K_{ex} denotes the equilibrium constant $[Q][O_2]/[QO][O]$. In the MIF phenomenon the δ^Q is the same for $Q = O^{17}$ and $Q = O^{18}$.

Key Experimental Results to be Explained by an MIF Theory

In attempting to understand the η-effect (MIF) in physical terms, we first recall several experimental results that a theory for the MIF should explain, results that would also constitute a test of any theory:

i) It is now well known that there are two distinct isotope effects in the MIF literature, one being the MIF. The other is an effect arising from the difference of zero-point energies of the two exit channels of a dissociating ABB* formed from A + BB, where A and B are different isotopes of O. In this second isotope effect (24, 25) the low-pressure recombination rate constants for the formation of ozone isotopologues ABB* from A + BB are studied under "isotopically unscrambled conditions" (8), namely, where an effort is made to avoid complications from follow-up reactions of the products of the dissociated ABB* with other species. It was shown (8–12) that this very interesting ΔZPE effect cancels under conditions ("isotopically scrambled conditions") where the MIF is studied experimentally and cancels for a physically understood reason. We return to this point later.

ii) As seen in Eq. **3**, four recombination rate constants and one equilibrium constant are needed to relate the MIF to individual recombination rate constants (8). The results for both $Q = O^{17}$ and O^{18} trace isotopes are needed to distinguish from some small mass-dependent component (24, 25) that also occurs. To calculate the ^{17}O and ^{18}O enrichment using some existing theory, for example ref. 26, one would need to pursue any such calculation further, because only three of the seven required rate constants were computed. This remark applies, of course, to other calculations in the literature as well.

iii) One major feature of the MIF is that it is a low-pressure phenomenon that disappears at higher pressures (6, 27, 28). At these low pressures, an equilibrium exists between $O + O_2$ and the accessible states of O_3^* for all isotopologues present. It was shown in ref. 8 that the particular combination of rate constants in Eq. **3** can be rewritten in terms of the steady-state density of accessible quantum states accessible by at least one of the atom–diatom channels of the excited ozone isotopologues. That work showed that the final expression for $^{\delta}\mathbf{Q}$ is independent of the ΔZPE effect.

iv) The effect of pressure in reducing the MIF (6, 27, 28) occurs at pressures that are considerably lower than the "Lindemann fall-off pressure" for the formation of ozone from $O + O_2$ (6, 29, 30) for the same added gases. (The Lindemann fall-off pressure is the pressure at which the unimolecular dissociation rate constant, and hence the bimolecular recombination rate constant, is 50% of its high-pressure value.) This major difference in the pressure effect indicates a difference in the role of the collisions in these two distinct phenomena.

v) For any ozone isotopologue the MIF is largely independent of the isotopic masses, as seen in the experiments of Mauersberger and coworkers for all of the isotologues (24, 28).

vi) The MIF decreases with decreasing temperature (28).

Although both types of isotope effects have been observed for ozone formation, one of them, the ΔZPE effect is, in our view, well understood both qualitatively and quantitatively in terms of transition state theory (RRKM theory) (8–12). It is an interesting effect and has also been the subject of a number of quantum mechanical scattering calculations (31–34). In the present overview of the MIF we confine our attention to the MIF effect itself. An excellent recent review of the isotopic fractionation of ozone for both effects is given by Feilberg et al. (6).

MIF, a Low-Pressure Effect

Some specific results on the effect of pressure of a third body M on MIF are available, although relatively sparse and in need of data at higher pressures. The difference between the pressure for the "50% Lindemann fall-off" of the rate constant for the three-body recombination or dissociation and the pressure of the same gas for the 50% decrease of the MIF from its low-pressure value is perhaps the most dramatic when the third body M is SF_6. The 50% Lindemann fall-off pressure for $M = SF_6$ occurs at ∼20 atm (30), whereas for the MIF the 50% value occurs at less than 0.5 atm (6). For $M = O_2$ or N_2/O_2 the respective numbers are ∼100 atm for the recombination rate (29) and ∼10 atm for the MIF (27, 28). Comparisons for other gases could also be made. The data are incomplete at the needed higher pressures. There is also some uncertainty in the 50% fall-off pressure for deactivation when additional complications occur at very high pressures (29), as judged by an unusual increase of the slope of one rate constant vs. the third-body pressure plot at high pressures (29).

From the existence of an MIF at low third-body pressures that greatly decreases with higher pressure we conclude that any theory of MIF should recognize both that it is a low-pressure phenomenon and that a quasi-equilibrium exists at low pressures, $O + O_2 \rightleftharpoons O_3^*$ between all isotopologues of O and O_2 and the accessible states of all isotopologues of O_3^*. Accordingly, any theory of the MIF needs to consider not only the forward step in O_3^* formation, but also the dissociation, to have a quasi-equilibrium at low pressures between the accessible states of all transient isotopic species.

Because the MIF η-effect is a low-pressure phenomenon, it can have one of two possible origins (8, 9): (*i*) an isotopic symmetry effect on the low-pressure $O + O_2 \rightleftharpoons O_3^*$ quasi-equilibrium constant associated with the quantum states of O_3^* accessible from $O + O_2$ or (*ii*) a difference in deactivation collisional cross-sections of the third body with symmetric compared with asymmetric isotopologues. The difference in collisional effect on recombination rate constants for isotopically symmetric and asymmetric molecules was calculated (35), but the theory was too approximate to draw conclusions for this possibility. Eventually, more accurate computations of the role of deactivating collisions would be of interest, particularly on what we later term "symmetry-changing collisions".

Accordingly, we focus on an intramolecular source of an MIF and consider it together with the possibility of explaining the large difference in pressure fall-off regions for the recombination and for MIF. One possibility for the latter is a difference in cross-sections between deactivating and symmetry-changing collisions. We return to this topic later. We first consider, briefly, several classical, semiclassical, and quantum aspects of intramolecular dynamics of isolated molecules (15–19) relevant to discussing a role of symmetry in the onset of "chaos" in intramolecular dynamics and in the MIF.

Classical, Semiclassical, and Quantum Intramolecular Dynamics

When the classical internal motion of a molecule is quasiperiodic ("regular"), a molecule having n coordinates and n momenta for the given energy lies in an n-dimensional subspace, a torus, at any given energy E, instead of on a phase space of $2n - 1$ dimensions available to the corresponding chaotic (statistical) molecule. A special example of a molecule that is regular is one whose vibrations are harmonic, with n constants of the motion, the so-called action variables (the classical counterparts of quantum numbers), but the introduction of some anharmonicity can still leave the motion quasi-periodic and hence restricted to motion on the n-dimensional subspace (Kolmogorov, Arnold, and Moser theorem) (15–18).

An ozone molecule that is in a quasiperiodic state cannot dissociate, dissociation being aperiodic. Correspondingly, such states would not be accessible by the reverse process of recombination (microscopic reversibility). Such molecules have fewer accessible states when formed from $O + O_2$ and so from a statistical point of view have a shorter lifetime. As a consequence, with less time to undergo deactivating collisions their rate of formation of O_3 would be less. N. Ghaderi in our group, using classical trajectories and methods outlined in ref. 36, found that (classically) about 10–15% of the O_3^* phase space did not dissociate and so had quasiperiodic orbits. However, quantum mechanically this restriction is not as severe, because semiclassically the system can undergo tunneling between the phase space tori. For the present, we simply assume that internal resonances will favor statistical theory, but this is just an assumption, albeit dynamically based. We note that some nonstatistical behavior is a necessary but not a sufficient condition for the MIF and also that, as discussed in this paper, because of the role of symmetry, the MIF is a quantum phenomenon and so there is no immediate link between the 10–15% of nondissociating trajectories mentioned above and the magnitude of the MIF.

Siebert et al. found classical periodic orbits at energies above the dissociation limit (37). Periodic orbits are a special case of quasiperiodic orbits with all frequencies commensurate. These frequencies vary with the classical mechanical phase space action variables and so each periodic orbit in phase space is encircled by quasi-periodic orbits, the whole constituting a classical resonance. In Chirikov theory (20) the overlapping of classical resonances leads to classical chaotic and hence statistical behavior (more bifurcations); Coriolis effects have also been implicated in slow intramolecular energy exchange (5, 38, 39), contributing to some deviation from statistical theory. The overall deviation from statistical theory for the recombination rate constant was (N. Ghaderi) less than a factor of 2. So, classically, the statistical model is not quite right for O_3^* but not far wrong. For the η-effect deviations of only 10–15%, and so only a relatively small deviation from a statistical behavior, but of the right kind, are needed for this effect.

Corresponding quantum mechanically to overlapping of classical resonances is the overlapping of avoided crossings of vibrational–rotational eigenvalues (40–42) that in turn make a state unidentifiable in a spectrum. Vibrational spectra of ozone have been measured up to ∼7,800 cm^{-1}, using cavity ring down spectroscopy, e.g., refs. 43 and 44, and numerous states identified for energies that are still substantially below the dissociation limit of ∼8,400 cm^{-1}, where vibrational anharmonicity and mixing of regular states would occur even more. There are many earlier studies of internal resonances in ozone, albeit with less resolution, e.g, refs. 45–50. We note here that even in a nonstatistical classical model for the dissociation of O_3^*, any ensemble of O_3^* molecules would not lie on a single torus, but rather would be distributed over many tori. A quantum state would occupy a phase space volume element h^N in N-dimensional phase space. Any chaos in the form of higher-order resonances within a volume element h^N would be coarse gained and so presumably not contribute to quantum chaos. In classical mechanics, in that volume element they may be many resonances and so many bifurcations of trajectories, yielding a classical chaos. In this case, quantum mechanics can yield regular states whereas the corresponding classical mechanics yield chaos.

This case would not be the first where an eigenvalue spectrum is more regular than that expected from classical trajectories. For example, Jaffe and Reinhardt (53) for the Henon–Heiles potential (52) used classical mechanical perturbation theory, a theory that tacitly assumes quasi-periodicity, to calculate semiclassical eigenvalues by calculating the classical mechanical vibrational action variables and quantizing them by semiclassical theory. They found good agreement with the quantum mechanical eigenvalues, even at high energies, where the system is classically chaotic, with pockets of quasi-periodicity. For the present we adopt the following model. Whereas overlapping resonances lead to statistical theory, nevertheless extensive resonances lead to extensive energy sharing and perhaps a largely statistical behavior. The higher the density of resonances, it is assumed, the more the overlap of resonances and so the more the statistical behavior. A laboratory experiment on the effect of density of states on the onset of chaos is given in Kim et al. (53).

We consider next the implications for isotopically symmetric and asymmetric ozone or other molecules. For isotopically symmetric isotopologues, one-half of the vibrational–rotational quantum states is forbidden by the Pauli exclusion principle. Because of this difference between the symmetric and the asymmetric isotopologues, there is a smaller density of states in the former, thereby a smaller number of resonances, and so (by assumption) a smaller amount of energy sharing. The simplest statistical interpretation is that those isotopically symmetric molecules have, thereby, shorter lifetimes and so are less apt to be deactivated by collisions before a redissociation.

One key question is whether such a model can explain the difference between the pressure effect for the MIF and that for the recombination rate. An isotopically symmetric O_3^* with identical isotopes for the end atoms is, in the presence of a nearby colliding gas molecule, no longer isotopically symmetrical and during the collision can change its rotational–vibrational state to permit the molecule to access otherwise nonaccessed states during its lifetime. E.g., if the rotational–vibrational state had one symmetry for the vibrations and, for the given isotopic spins, the appropriate symmetry for the rotations, then after the collisions these rotational–vibrational symmetries can be reversed. One can term the collisions "symmetry-changing collisions". When they occur frequently enough during the lifetime of the O_3^*, all vibrational states of any particular O_3^* can be accessed and not just one-half of them. If such state-changing collisions have a cross-section significantly larger than that for deactivating collisions, then the lower fall-off pressure for MIF compared with that for recombination can be understood. Clearly, relevant quantum mechanical computations on collision cross-sections will be instructive. There has been extensive study of conventional energy transfer collisions (e.g. refs. 54 and 55), and perhaps these methods can be adapted to symmetry-changing collisions.

One feature not discussed thus far is the effect of temperature on the MIF (56, 57). In treating an effect of temperature on the recombination rate for the $O + O_2$ reaction Troe introduced a chaperon mechanism (29, 30, 58), in addition to the energy transfer

mechanism, the importance of the chaperon component increasing with decreasing temperature. In this mechanism, the third body M serves as a chaperon closely bound to one of the reactants, e.g., $O_2 + M \rightleftharpoons O_2M$, followed by reaction $O_2M + O \rightarrow O_3 + M$, the M carrying away some of the excess energy. The decrease of the MIF with decreasing temperature (56, 57), we suggested (59), may be due to an increasing contribution of the chaperon mechanism at low temperatures, because for a chaperon mechanism there is no long-lived quasi-equilibrium $O + O_2 \rightleftharpoons O_3^*$ and so in the present theory no MIF. It has been estimated that the major component of the three-body recombination at low temperature occurs via a chaperon mechanism (29, 58, 60). One can expect, as a consequence, that the discrepancy between the fall-off pressure for MIF and that for MIF will decrease when the temperature is decreased.

To learn more experimentally about the distribution of lifetimes of O_3^* molecules, one possibility would be pump-dump laser experiments in which a ground electronic state O_3 molecule is excited to a repulsive electronic state and then with a second laser is dumped into the ground electronic state of the molecule, but with enough energy to dissociate. One might explore testing whether all such isolated molecules dissociate, even the quasi-periodic ones because of tunneling, and particularly whether the decay is single exponential (statistical) or multi-exponential (nonstatistical) and whether there are some residual nonstatistical O_3^*s that do not dissociate.

There has been a start on quantum mechanical computations for MIF in ozone formation (59–62), and a mixed quantum-classical calculation is given in ref. 25. Rigorous computations are extremely demanding and presently incomplete. The full-scale quantum dynamics would treat MIF using the numerous angular momentum states of the colliding $O + O_2$ reactants, including a treatment of the newly formed long-lived O_3^* living perhaps 100 ns at the pressures involved in MIF, which treats for the reacting system the appropriate symmetry restrictions, as well as the three-body collision aspect. Such a treatment is still on the horizon. Examples of some calculations are given in refs. 25, 34, and 61–63. A number of computational studies have been made, instead, of the quantum mechanics of the isotope ΔZPE effect. As noted earlier, this isotope effect cancels in "scrambled systems" (8), systems where the MIF effect is actually observed in experiments, and so theories of the ΔZPE effect are interesting in their own right but not revealing in my view for understanding the MIF. We noted that the ΔZPE effect cancels exactly for the MIF. The reason is that, at the low pressures involved, there is an equilibrium between the states of all the isotopologues of O_3^* and the two sets of reactants in the two exit channels. Some of the O_3^* states are accessed from one channel and some from the other, but there is quasi-equilibrium.

As noted earlier to treat the MIF quantum mechanically four rate constants are involved for each of ^{17}O and ^{18}O enrichments (8, 9). Of particular value in MIF-focused quantum calculations is the treatment of A + AA collisions, because there is then no complication due to the unneeded ΔZPE. It is absent in this case. The effect of symmetry can be studied using the same masses for the three isotopes, but using distinguishing labels, and so investigating the pure symmetry effect in the absence of a ΔZPE. An example of subtle differences in symmetry effects is found in a detailed study of a much simpler system, the $Ne_2 + H \rightarrow 2Ne + H$ system (64).

In summary, we have considered a possible origin for the MIF in terms of the relative nonstatistical behavior of symmetric and asymmetric isotopologues and suggested potential experiments and computations.

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